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REFINERY EFFLUENT WATER TREATMENT PLANT USING ACTIVATED CARBON

Gary C. Loop

Atlantic Richfield Hanford Company

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Robert S. Kirr Environmental Research Laboratory

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The carbon was exhausted at the rate of 9.5 pounds per 1000 gallons of water processed. At an average feed COD concentration of 250 ppm and an average effluent COD concentration of 50 ppm, the carbon was loaded to an average of 0.26 pounds of COD per pound of carbon. Following solution of initial startup problems, the unit was operated at a cost of 40 cents per 1000 gallons of water treated, or 18 cents per pound of COD removed.

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By

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Reduction of Chemical Oxygen Demand (COD) in petroleum refinery effluent wastewater by adsorption onto activated carbon was demonstrated on a commercial level during a two-year project at Carson, California. The plant contained over 750,000 pounds of carbon, regenerated 1,644,000 pounds of carbon, processed 172 million gallons of water, and removed 408,000 pounds of COD.

The carbon was exhausted at the rate of 9.5 pounds per 1000 gallons of water processed. At an average feed COD concentration of 250 ppm and an average effluent COD concentration of 50 ppm, the carbon was loaded to an average of 0.26 pounds of COD per pound of carbon. Following solution of initial startup problems, the unit was operated at a cost of 40 cents per 1000 gallons of water treated, or 18 cents per pound of COD removed.

This report was submitted in fulfillment of EPA Grant No. 12050 GTR, under the partial sponsorship of the Environmental Protection Agency. Work was completed by Atlantic Richfield Company, Carson, California, January 1974.

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Mr. Gary G. Loop, Associate Process Engineer, provided technical direction and prepared the final report.

Mr. E. F. Dumas, Refinery Technology Supervisor, and Mr. P. L. Mehta, Process Design Engineering Supervisor, provided required technical assistance.

Mr. R. P. Strand, Waste Water Disposal Supervisor, provided operational guidance of the plant.

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The Environmental Protection Agency provided partial financial support, and Mr. Leon H. Myers, Project Officer, provided necessary guidance.

SECTION I

CONCLUSIONS

1. Reduction of Chemical Oxygen Demand (COD) content in refinery waste water effluent has been demonstrated to be feasible by using activated carbon as an adsorbent.

2. The system performed well in that it demonstrated an ability to start up and shut down without delay or difficulty. This gives the process a distinct advantage over biological units for use in handling intermittent rainfall.

3. During the two-year project the unit was operated at an overall average cost of 49 cents per 1000 gallons of water treated or 24 cents per pound of COD removed from the effluent waste water. The first year's operational costs were 62 cents per 1000 gallons of water treated, or 34 cents per pound of COD removed. After improvements over the first year's operation, the costs during the second year were reduced to 40 cents per 1000 gallons of water treated, or 18 cents per pound of COD removed.

4. The plant demonstrated excellent reliability.

5. The carbon adsorption plant has demonstrated that when the feed COD is controlled to an average of 233 ppm, the plant can treat refinery water using 8.5 pounds of carbon per 1000 gallons treated and reduce the effluent COD to an average of 48 ppm with a high level of 95 ppm.

SECTION II

RECOMMENDATIONS

This project demonstrated that activated carbon can be used on a commercial scale to reduce the Chemical Oxygen Demand (COD) concentration of petroleum refinery effluent waste waters. However, several areas need further investigation. These are summarized below.

1. Further determination of the quantities and types of COD materials that do and do not adsorb onto activated carbon.
2. Determine feasibility of pretreatment to reduce load on carbon.
3. Determine optimum number of stages in adsorption process with controlled feed COD concentrations.

Variables to consider when constructing commercial plant:

1. Be certain that desired effluent COD concentration is attainable for the particular circumstances involved. This should be done by use of a pilot plant representative of the commercial plant.
2. The feed COD concentration range should be determined and controlled to eliminate surges. This could be done by recycling effluent water, or possibly by some pretreatment facility.

SECTION III

INTRODUCTION

Petroleum refineries are faced with the problem of disposing of hugh volumes of waste water. These large amounts of water come from a wide variety of sources. These sources include process water used for heat transfer, wash water, and rain water runoff which collects oils and chemicals from within the refinery.

In the past, separation of the visible, floatable oils were considered satisfactory to allow discharge into adjacent waterways. However, new concern over the ecological balance of our environment has called this practice into question. In an effort to protect our waterways from these harmful discharges, new and improved technology is needed.

One major pollutant existing in refinery discharge waters is oxygen demanding material. Oxygen demand, which refers to the demand for oxygen by chemicals and oils, lowers the water's available dissolved oxygen content, a vital need for marine life.

In 1968, the Los Angeles Regional Water Quality Control Board made a study of the Dominguez Channel in Los Angeles County. They determined that petroleum and chemical plant discharges were causing a problem due to their oxygen demand. The Control Board, in accordance with these findings, issued a resolution in February 1968, which limited the total chemical oxygen demand (COD) from all industrial discharges into the Channel. These discharges included rain water runoff. The resolution was to be complied with by February 1971.

Atlantic Richfield Company's Watson Refinery is one of about 16 industrial facilities discharging water into the Dominguez Channel. As defined by the resolution, the Watson Refinery was limited to 1330 pounds per day of COD in its discharge water to the Channel. Meeting this requirement meant reducing the COD in its discharge waters by 95% if the water was discharged to the Channel.

The Watson Refinery, as a taxpayer of Los Angeles County, made an agreement with the Los Angeles County Sewer District to have its process waste water handled in the County's primary treatment unit. However, due to limitations in the County unit, the County was unable to handle rain water runoff. This presented a problem for the Watson Refinery due to the fact that the rain water collection facilities were interconnected with the process waste water collection system. Therefore, during periods of rainfall, the process waste water and rain water mixture could not be sent to the sewer district facilities due to the presence of rain water, nor could it be sent to the Dominguez Channel due to high COD content of the process waste water.

To solve this problem a system was needed which would treat all the process water plus rain water as it was produced, or an impounding plus processing system which would allow large volume impounding during the rain followed by low volume processing. In either case, a system was needed which could be started up easily when rain fell and then shut down when no longer required. A biological unit requires continuous feed and thus the conventional technology of today was not satisfactory. Therefore, it was decided to use impounding followed by activated carbon treatment to adsorb the COD material from the impounded rain diluted process water.

Construction of the first commercial sized carbon adsorption plant for treatment of petroleum refinery waste water was completed in

1971 and contained over one-half million pounds of activated carbon. This report describes the first two year's operation of the unit and is submitted in fullfillment of Project Number 12050 GTR under the sponsorship of the Water Quality Research Division of Applied Science and Technology of the Environmental Protection Agency.

The specific objectives of the project were:

1. Determine feasibility of activated carbon as a treatment system for storm water runoff and refinery process waters.
2. Evaluate performance of the system.
3. Determine operating costs.
4. Assess reliability of the system.

SECTION IV

PROCESS DESCRIPTION

ADSORPTION

Adsorption is defined as physical attraction of molecules onto a surface, such as the pore struction of activated carbon. Activated carbon is carbon that has been processed to obtain surface areas in the order of 1,000 square meters per gram by penetrating the particules with molecular size pores. The total surface area is essentially unchanged even by grinding the material to a fine powder, as the surface area of the outside of the particule is small compared to the pore surface area.

Strong adsorption takes place by capillary effect as the pore size nears the size of the molecules adsorbed. Dissolved organics are generally more strongly adsorbed than inorganic compounds. Higher molecular weight compounds generally displace the lower molecular weight compounds in the pores. Non-polar compounds are usually more strongly adsorbed than polar compounds, and they will also displace the polar materials. These and other factors, influence the net adsorption effect under flow condition in a granular activated carbon bed.

Activated carbon was used during the two-year project to adsorb organic chemical oxygen demand materials from the impounded rain water and process water mixture. Filtrasorb 300, the adsorbent used for the Watson Carbon adsorption Plant, is an activated carbon with granules having an approximate size range of 8 to 30 mesh made from bituminous coal. It is made to high hardness standards

to minimize attrition loss in handling, regeneration, and hydraulic transport. It has a broad spectrum of pore sizes to meet adsorption requirements for a braod range of organic molecule sizes.

THERMAL REGENERATION

Filtrasorb 300 is regenerated by selective oxidation of the organic impurities in the pores. This is done at high temperatures (1600°F-1750°F) and with a controlled low oxygen atmosphere in a multiple hearth furnace. As the carbon is heated, the more volatile organic compounds are vaporized. With further heating additional organics are pyrolysed. The remaining organics are then oxidized selectively by addition of air. The carbon is then quenched in water. Time, temperature, and atmosphere are the controllable parameters for regeneration. Free oxygen must be carefully controlled in the lower hearths of the furnace to avoid burning up the regenerated carbon.

CHLORINATION

As there is an inorganic COD background level in the total COD, provision was made for chlorination after adsorption. Chlorine can be added to the effluent stream to permit operating the carbon beds with some breakthrough of organics as chlorine will reduce organic COD level as well as inorganic. This provides greater flexibility in loading the carbon or in handling an unusual COD load.

SECTION V

DESCRIPTION OF ACTIVATED CARBON PLANT

The water treatment facility is made up of four main systems plus an impounding reservoir. Figure 1 describes this system. An overall view of the adsorption plant is given in Figure 2.

RESERVOIR

The reservoir is a 1.2 million barrel holding basin which impounds all refinery waste water and rain water runoff when the Los Angeles County Sewer District will not accept it. The reservoir is shown in Figure 3.

WATER TREATMENT CARBON ADSORPTION UNIT

The water treatment unit is shown in Figure 4. This unit reduces the organic COD of water impounded in the refinery prior to discharge to the channel. The water treatment unit consists of twelve identical adsorber cells, (V-1 through V-12), each 12' x 12' x 23' deep. Each cell originally contained a 13' deep bed of carbon having a dry weight of approximately 48,700 pounds. Supporting the carbon bed is a one-foot layer of gravel on top of a Leopold underdrain system. The depth of the carbon was altered in 1972 for reasons discussed later in this report.

Impounded water is delivered to the influent water distribution trough through a 14" line from the impounding reservoir. The water is distributed to any or all of the twelve adsorber cells (V-1 through V-12) by slide gates. Flow to each cell is regulated by a handwheel operated slide gate.

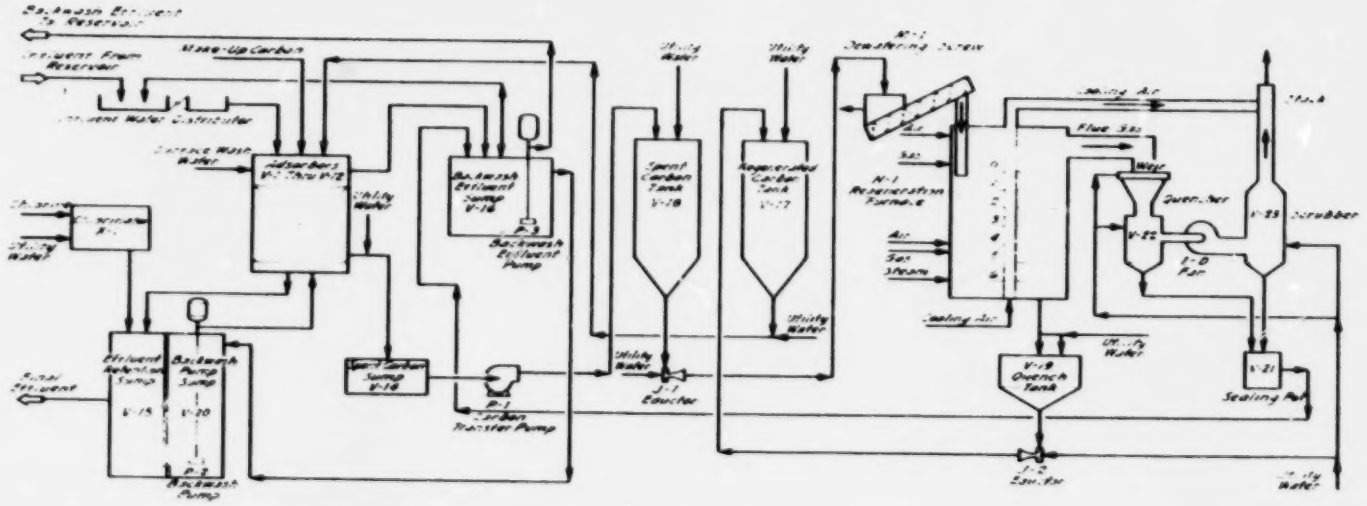

Figure 1. Carbon Adsorption Plant
Flow Diagram

Figure 2. Overall view of Carbon Plant

Figure 3. Impounding Reservoir

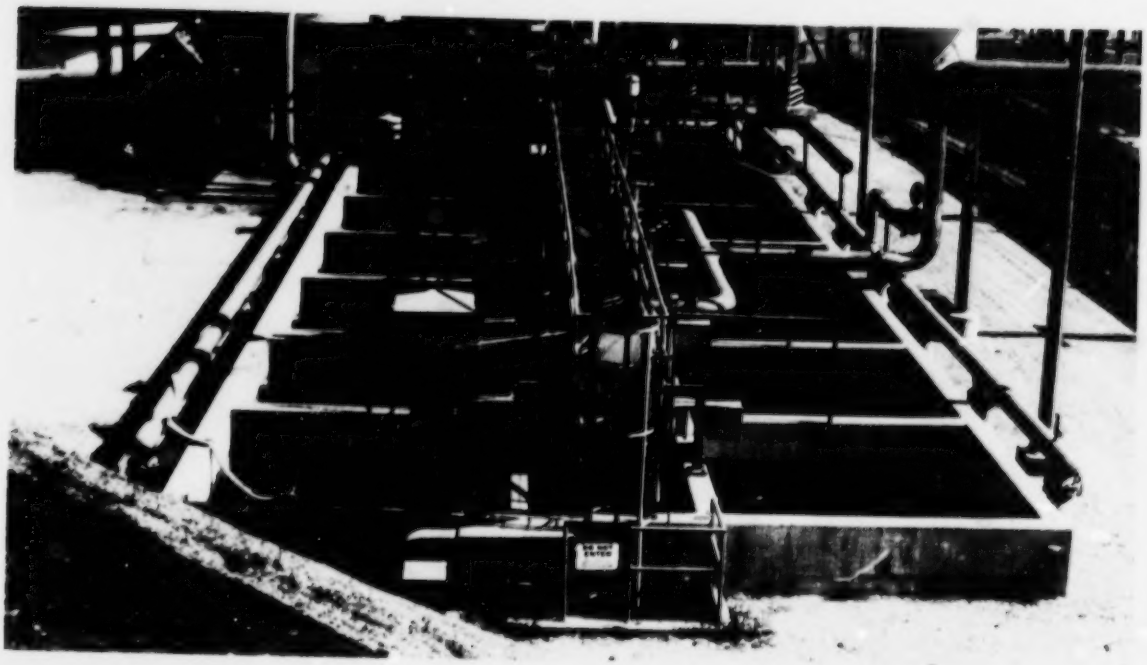

Figure 4. Water Treatment Unit

The waste water first hits a splash plate designed to prevent packing or pocketing of the bed. A view into an adsorber cell is shown in Figure 5. The water level will be above the surface of the carbon bed, and the level varies depending on flow rate and pressure drop from solids accumulation on the bed. The water passes down through the carbon bed where it collects in the underdrain system.

The treated water flows through 6" lines from each cell to a 24" collection header leading to the effluent retention sump (V-15). Each 6" cell discharge line has a sample point and an air-operated pinch valve which can be shut during backwashing.

A chlorine-water solution may be injected into the incoming treated water stream at the inlet to the effluent retention sump (V-15). Approximately 15 minutes retention time is allowed for chlorine contact in this sump. The chlorinator (X-1) injection rate is manually adjusted to further reduce the COD content. The treated water collected in sump V-15 overflows through a 24" underground drain through an outfall box to the channel.

BACKWASH

Each carbon bed must be backwashed whenever it will not pass its share of water flow due to buildup of solids on top of the carbon. Frequency of backwashing depends on the rate of build-up of solids on the carbon bed. A bed is backwashed whenever it will not pass its share of water flow. When this occurs, flow from the bed is stopped by closing the pinch valve on the 6" discharge line. Treated effluent is pumped (P-2) from the backwash sump (V-20) up through the bed to expand the bed and flush out accumulated solids. Surface washers, which spray water from nozzels on a pipe rotating just above the carbon bed, will enhance this action. Bed expansion is affected by flow rate, water temperature, density, organic

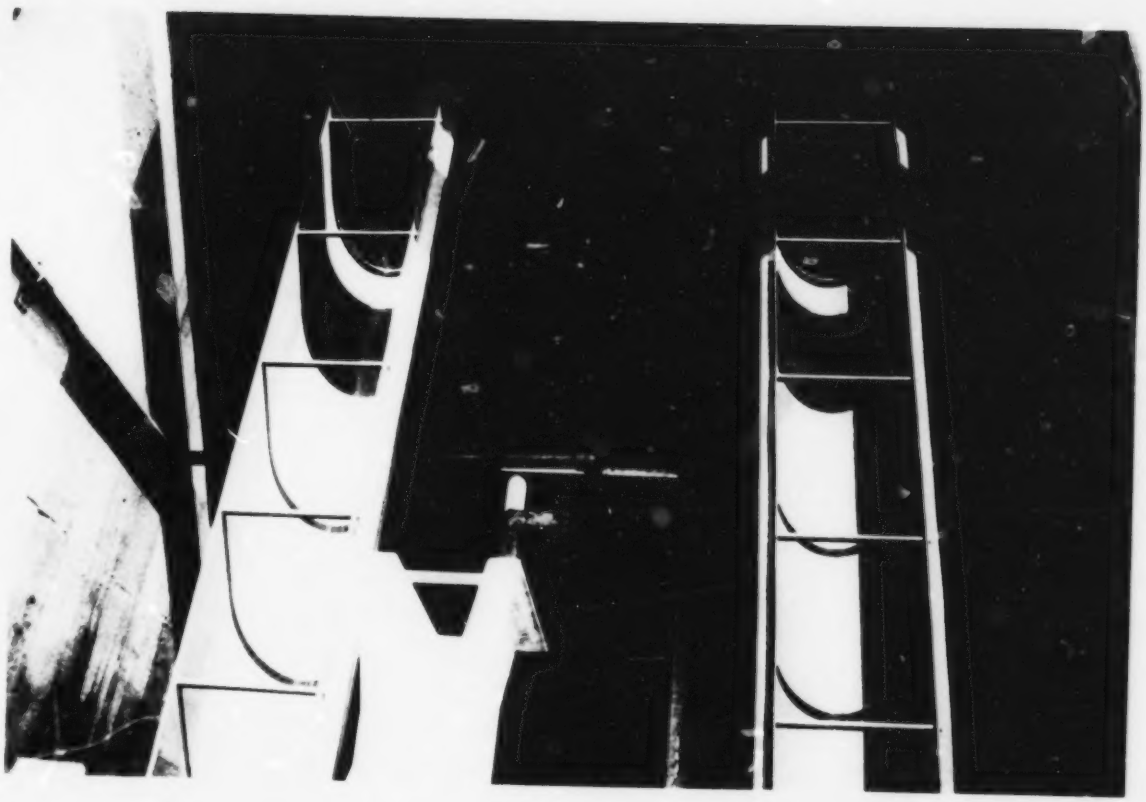

Figure 5. View Into An Adsorber Cell

loading, and surface wash action. The turbid water overflows into the backwash troughs to the backwash effluent sump (V-16). From there it is pumped (P-3) back to the reservoir for settling and retreating.

CARBON HANDLING SYSTEM

The carbon handling system includes the storage tanks for spent carbon (V-18), and regenerated carbon (V-17); plus the pump, eductor, piping, and controls to move spent carbon from any cell to tank V-18, and regenerated carbon from V-17 back to any cell. The storage tanks are shown in Figure 6.

When the carbon in a bed is exhausted, the flow of water is stopped, the spent carbon removed, and the bed refilled with regenerated carbon. After a backwashing to remove fines and to stratify and level the bed, the flow of water is restarted.

The spent carbon is removed from the bed as a water slurry through a valve in the side of the adsorber cell. The carbon slurry flows by gravity in a concrete trench to the suction of the spent carbon transfer pump (P-1). The carbon slurry is transferred by pump (P-1) to the spent carbon tank (V-18) where it is stored prior to regeneration.

Regenerated carbon slurry is transferred by gravity from its storage tank (V-17) via hose to the proper cell. Utility water is added to assist the transfer.

REGENERATION FURNIACE

The regeneration furnace and gas scrubber are shown in Figure 7. The slurry of spent carbon is delivered from the bottom of its storage tank (V-18) to the dewatering screw (M-1) at a controlled rate. Motive water is provided from the utility system to eductor J-1. To maintain a constant carbon delivery rate, the water level in the spent carbon tank (V-18) is kept constant. The carbon

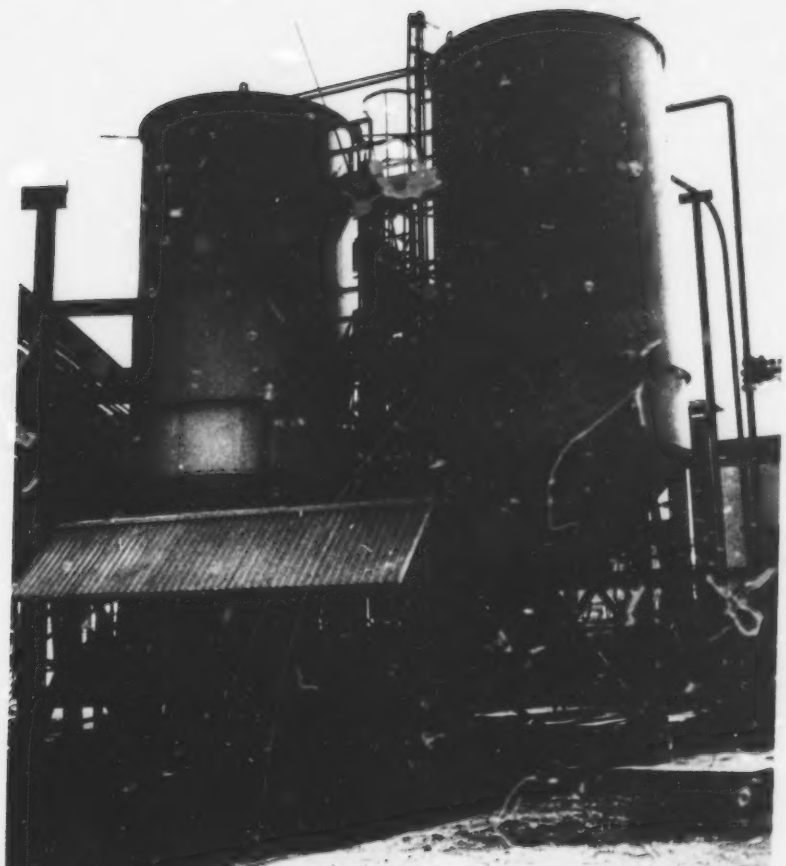

Figure 6. Carbon Storage Tanks

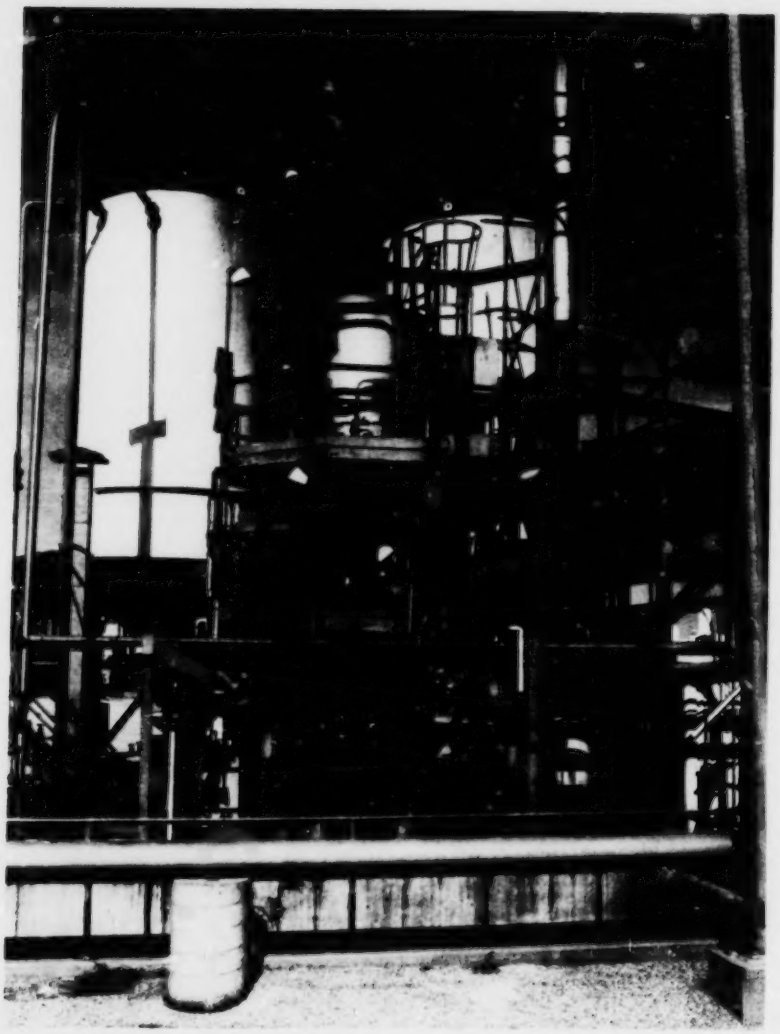

Figure 7. Carbon Regeneration Furnace and Gas Scrubber

settles out from the slurry in the feed end of the dewatering screw (M-1) located above the furnace. The dewatering screw is set at an angle so that the water drains from the unit counter-current to the flow of carbon. The drained carbon discharging into the furnace contains approximately 50% water (wet basis). Excess water overflows from the dewatering screw and is returned to the reservoir. The dewatered carbon flows by gravity from the dewatering screw to the top hearth of the regeneration furnace.

The regeneration furnace is a 56" I.D., six hearth multiple hearth unit. A diagram of the furnace is shown in Figure 8. It is gas-fired on two hearths. Supplemental air and steam are added on two hearths. A center shaft rotates arms with teeth which move the carbon across the hearths and downward through the furnace. The burners on the furnace automatically control furnace temperatures at the desired levels via thermocouple element and controllers. Steam and air addition rates are manually set.

The afterburner section is separately gas-fired to raise off-gas temperatures to about 1450°F. This is required to combust organic vapors in the furnace exit gas.

The hot gas from the after burner goes through a quencher where it is cooled by water injection, is pulled through induced draft fan (K-4) again with water injection for scrubbing, and exits through an entrainment separator where entrained water and particulate matter scrubbed out of the off-gases are removed. The clean flue gases are exhausted via stack to the atmosphere. Hot air from the center shaft is added to the stack to reduce the humidity and minimize the vapor plume.

Regenerated carbon discharges down a chute from the furnace in periodic slugs as the rabble arms pass over the drop hole on the bottom hearth. This chute has two legs. Normal carbon flow is

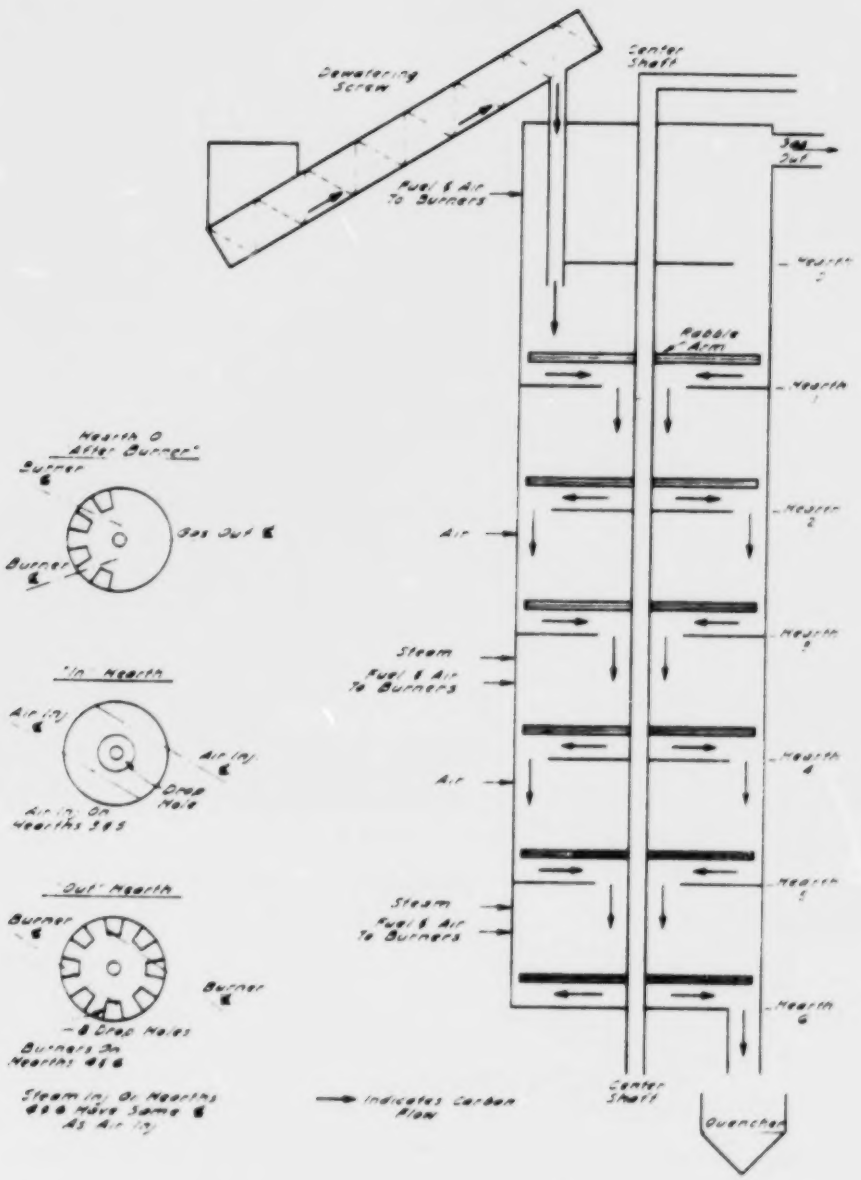

Figure 8. Carbon Regeneration Furnace

vertically into the quench tank (V-19). Water level in the quench tank is kept above the bottom of the chute to prevent air from being drawn into the furnace. A trash screen is provided in the quench tank to protect the eductor.

The 45° leg on the furnace discharge chute is used to bypass the quench tank in case transfer problems are encountered. Opening the dump gate permits hot carbon to drop directly into drums and allows continued furnace operation.

Water sprays are provided to quench the hot carbon to eliminate sudden evolution of steam which would upset furnace pressures. Quenched carbon is educted to the regenerated carbon tank (V-17) where it is stored until needed for refilling an adsorber cell.

SECTION VI

DESIGN BASIS

The volume of carbon in the adsorbers and its exhaustion rate are set by the volume of waste water to be treated, the concentration and types of adsorbable material in the influent, and the permissible COD concentration in the effluent water. Design of the full scale unit was based on pilot tests performed on diluted refinery waste water.

The carbon exhaustion rate was difficult to establish from the pilot plant tests because the influent COD concentration varied considerably, both above and below the limits expected under actual operating conditions. The actual design of the unit was based on the following criteria:

30 days per year of rain (maximum)
300,000 barrels water per rainy day (maximum)
9,000,000 barrels of water per year (maximum)
250 ppm COD average influent concentration
37 ppm COD average effluent concentration
1 pound of carbon exhausted per 1000 gallons water treated

Based on these criteria, the unit was designed to handle 100,000 barrels of water per day. Thus, the unit would run 90 days if the maximum rains were received without having to replace or regenerate any carbon. Based on this operation premise, regeneration of all carbon would be done during the summer, non-rainy season.

The regenerator furnace was designed to regenerate 8,500 pounds of carbon per day. This is equivalent to 11.3 GPM of slurry from V-18. The approximate utility consumption, based on design, was as follows:

Steam - 1.0 lb. of steam per lb. of carbon = 354 lbs./hr.

Refinery fuel gas (including afterburner = 3,000 SCFH

SECTION VII

OPERATION AND EVALUATION OF WATER TREATMENT FACILITIES

This section of the report covers the operation and evaluation of the adsorber cells and backwashing facilities.

FIRST PERIOD OF OPERATION

The first period of operation covers the first year from May 1971, through June 1972.

Initial Operation

The unit was first started in May 1971. The purpose was to test operation of the unit prior to the rainy season. Test water was synthesized by mixing high COD process water with service water and impounding. Impounded water was fed to cell 3 at the design rate of 250 GPM. With a feed COD of 650 ppm, the effluent remained in the 44-80 ppm range for the 208 hour run. In addition to the COD's being above the design level of 37 ppm, the effluent water was cloudy and had a septic odor. This condition of the effluent was believed to be caused by anaerobic bacteria growing on the carbon.

Caustic Treatment of Carbon Beds

It was decided to caustic wash four beds in order to kill the bacteria and improve COD removal efficiency. The beds were backwashed with 2% caustic until a pH of 11 broke through the bed surface. A white precipitate formed, a sour smelling gas was evolved, and the wash solution had a yellow color. The white

precipitate was easily backwashed out, and is believed to have been a carbonate compound. The sour gas is believed to have been H_2S, and the yellow color is believed to have been hydrocarbons released from the carbon and dissolved in the caustic solution.

A test with the four treated cells in parallel with four untreated cells was run for 21 hours to determine the effect of the caustic wash. The results are given in Figure 9. Although the effluent COD's were almost identical for the treated and untreated cells, the treated cells had very little problem with odor and clarity in the effluent water.

Because of the improved odor and clarity of the water from the caustic treated cells, all 12 cells were treated. With continued operation it was soon apparent that the adsorption plant was not adsorbing as much as expected.

Backwashing

Since the carbon was not adsorbing the COD in the amounts it had in pilot plant work, it was felt that trapped air might be decreasing the available surface area on the carbon. In an attempt to decrease the trapped air, a more vigorous backwash was used for three cells. The backwash rate was increased from 3,300 GPM to 5,000 GPM, which resulted in an increased bed expansion from 20% to 50%.

Although the effluent COD's were temporarily reduced to below 30 ppm, the improvement lasted only one day. The results from cell three are shown in Table 1. Since the increased backwash rate showed no permanent improvement, it was discontinued.

The frequency of backwashing was studied during the test runs described below. In run 4, backwashing was infrequent, while in run 5 the cells were backwashed daily. Despite a lower feed rate and lower feed COD in run 5, both run 5 and run 4 had equal effluent

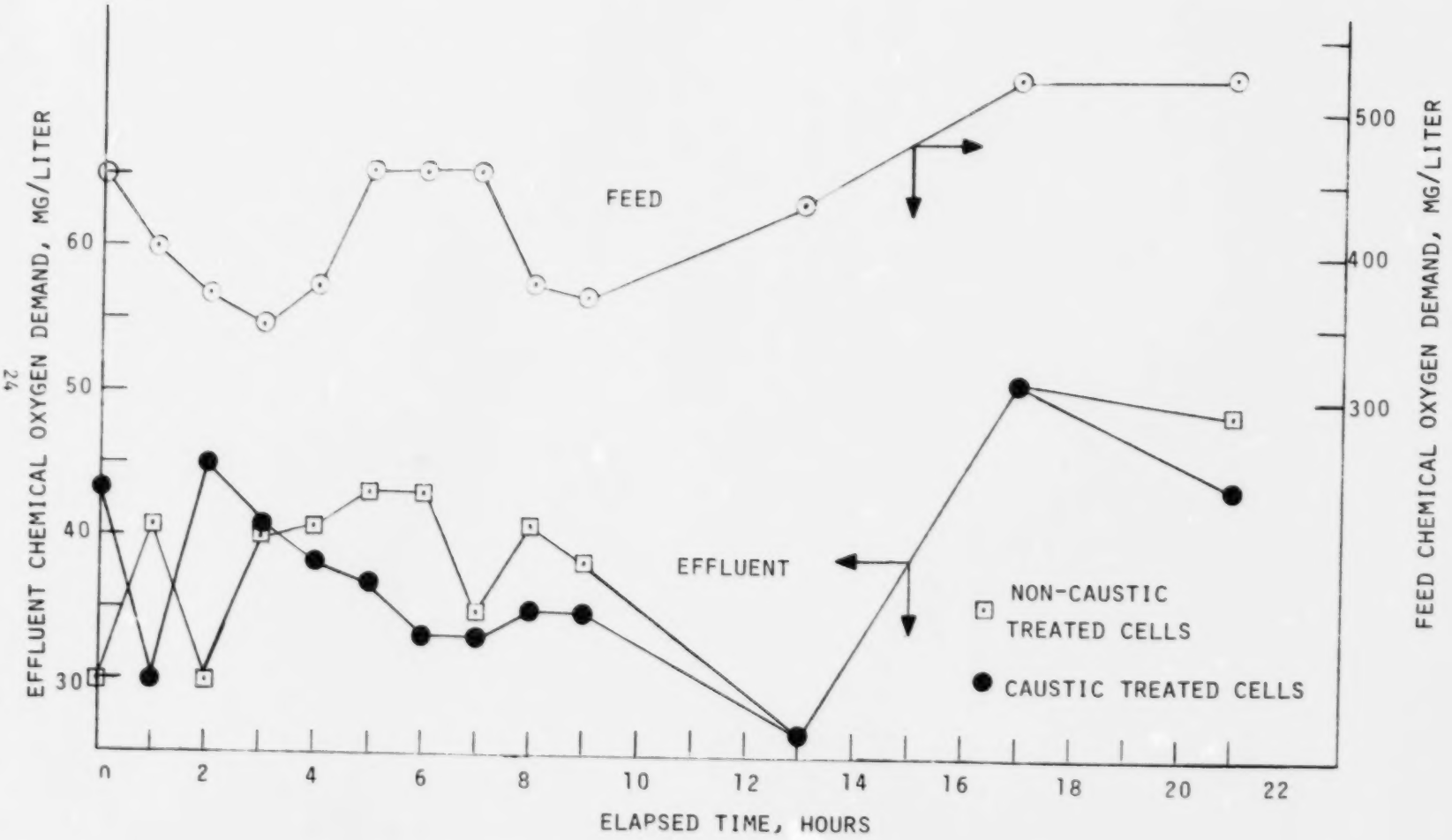

Figure 9. Caustic Treating Test Run

Table 1. COD DATA BEFORE AND AFTER VIGOROUS BACKWASHING AT 5000 GPM

CELL NO. 3

FEED RATE = 250 GPM

DATE	TIME	FEED ppm	EFFLUENT ppm
9-15-71	11:00 AM	194	83
	1:00 PM	189	89
	3:00 PM	264	114
9-24-71	11:45 AM & 12:45 PM backwashed @ 5000 GPM		
	For 10 and 11 minutes respectively		
	3:00 PM	75	<30
	6:00 PM	--	42
	7:30 PM	167	53
	11:00 PM	119	72
9-25-71	7:00 AM	119	76
	3:00 PM	113	74
	11:00 PM	116	77
9-26-71	7:00 AM	181	33
	11:00 PM	118	76

COD's. Increased frequency of backwashing is not felt to be an improvement for COD removal.

COD Penetration Into Carbon Bed

Cell number three was stopped after 208 hours of operation to study the problem of high effluent COD. Besides the testing of caustic washes and backwashing, data was collected to determine the relative efficiency at various depths in the carbon bed. The data is shown in Figure 10. The relative efficiency test, which is described in Appendix B, is an indication of the carbon's ability to adsorb COD compared with virgin carbon. The reliability of the test is discussed in the "Test Methods and Their Evaluation" section of this report. The data in Figure 10 indicates that the top two feet of carbon were completely exhausted while the last five feet were still at 65% of virgin adsorption ability.

Exhaustion Run

Cell three was run for 247 more hours during which time the plant was stopped once on September 17, 1971, and restarted again on September 24, 1971. The results for the last 247 hours are shown in Figure 11. During the seven days the plant was down, the feed COD decreased about 180 ppm. It appears that natural oxidation reduced the COD in the impounding reservoir.

Cell three was regenerated when feed and effluent COD's converged in the 431st hour. The exhaustion rate could not be calculated because by design criteria the bed is exhausted when the effluent COD exceeds 37 ppm. The effluent was rarely below 40 ppm. Based on the entire run, the carbon was used at the rate of seven pounds of carbon per 1,000 gallons of water treated.

Varying Flow Rates

As rainfall was extremely light, there was very little water processed by the carbon plant in the winter of 1971 and 1972. In addition to the light rainfall, the sanitation district accepted

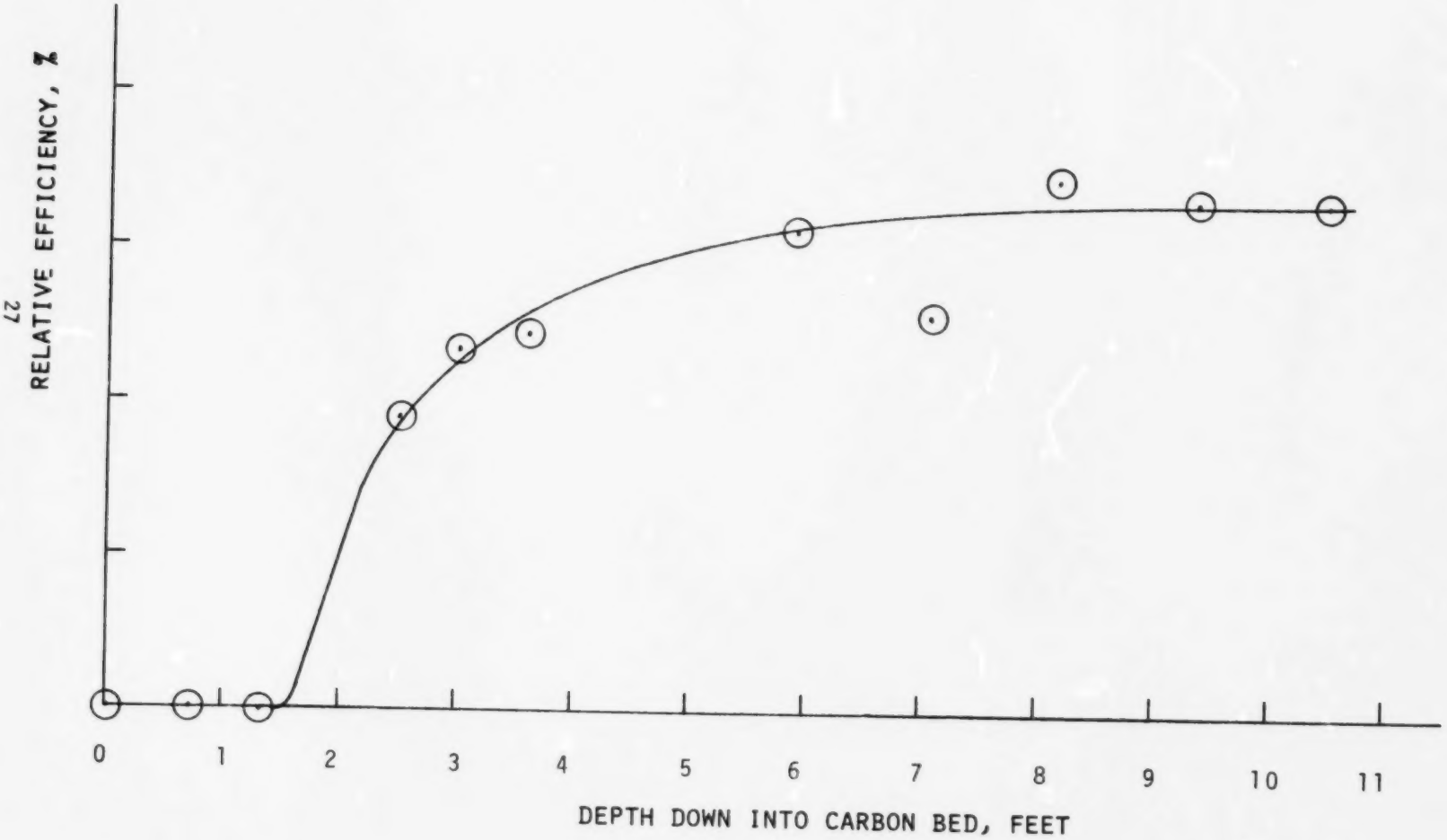

Figure 10. Relative Efficiency Profile of Cell No. 3 After 208 Hours at 250 GPM
650 to 600 PPM COD In Feed

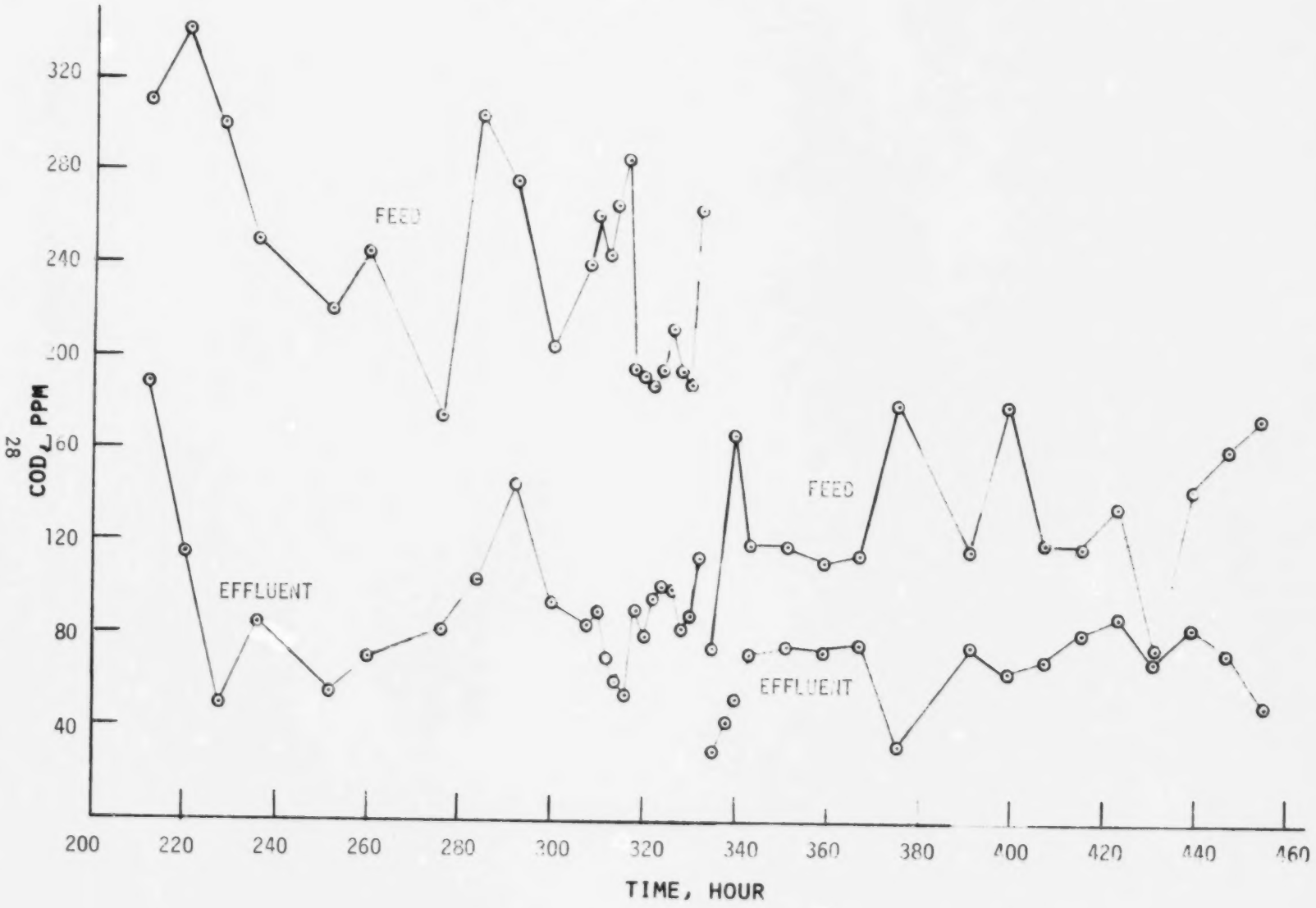

Figure 11. Cell Number Three COD Vs Time First Rains

process waters with COD's above 450 ppm 24 hours after rainfall stopped. Therefore, water was only processed when there was water in the impounding reservoir with a COD below 450 ppm. Throughout the winter, six runs were made with varying flow rates. Data from the six runs is given in Figure 12.

Run 1

The carbon plant was started at 4 p.m. on December 25, 1971, with a design feed rate of 3,000 GPM. All 12 cells were in service. The run lasted 44 hours with an average feed COD of 326 ppm and an average effluent COD of 43 ppm. The run was stopped when the feed COD jumped above 450 ppm. During this run, samples of feed and effluent were tested for COD, turbidity, color, odor, and suspended solids. The results of these tests are listed in Table 2.

Run 2

Run 2 was started when the feed COD dropped to 415 ppm. This run which lasted 47.5 hours had an average feed COD of 360 ppm and an average effluent COD of 48 ppm. Halfway through the run, the rate was reduced to 2,000 GPM to comply with channel discharge limitations.

Run 3

Again 2,000 GPM was continued as effluent COD's average 80 ppm. The feed averaged 374 ppm and the run lasted 38.5 hours.

Run 4

The fourth run lasted only 18 hours with a feed rate of 2,000 GPM. The average feed COD was 310 ppm and the effluent averaged 67 ppm.

Run 5

The effluent was still well above 37 ppm COD with an average COD of 66 ppm. The feed rate was cut to 1,000 GPM to assure compliance with the COD discharge limitation. The feed averaged

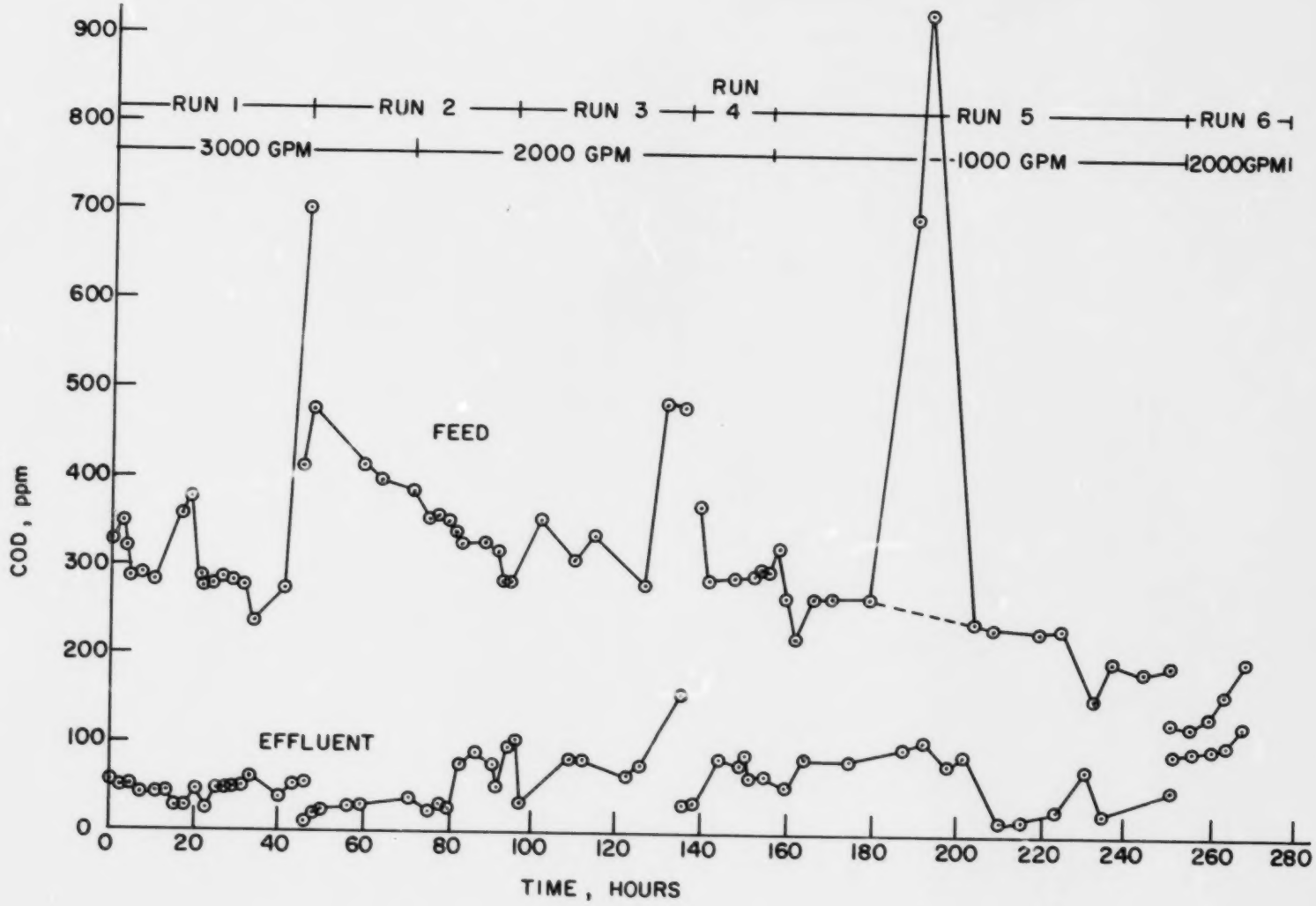

Figure 12. Feed and Effluent COD Data First Rains

Table 2. LABORATORY DATA ON CARBON PLANT FEED AND EFFLUENT

Date	COD	Turbidity J.T.U.	Color	Odor	Total Suspended Solids, ppm
Feeds					
12-27-71	690	56	65	8	122
12-28-71	415	41	72	8	64
12-29-71	370	36	60	12	132
Effluent					
12-27-71	43	14	11	1	11
12-28-71	15	14	15	1	20
12-29-71	40	12	13	1	34

237 ppm COD if the extremely high peak in Figure 12 of 900 ppm COD is discredited. This was the longest of the six runs and lasted 95 hours.

Run 6

Run six lasted 22 hours with an average feed COD of 147 ppm. Although the feed COD was low, it had a green algae which was not adsorbed or filtered by the carbon bed. The effluent which averaged 93 ppm COD was also green in color. The problem with algae occurred again during later testing and is discussed under the "Two-State Test Run" heading of this section.

Evaluation of First Rain's Operation

Despite several attempts to improve operation, the carbon adsorption plant was unable to process water at the design rate of 100,000 barrels per day, and still meet county regulations. Fortunately, rains were light, and the sanitation district accepted high COD water.

The COD loadings of each cell vs. gallons of water treated are given in Figures 13 through 18. The loadings varied from 0.2 pounds of COD per pound of carbon to about 0.3, at the end of the first rainy season. Since the effluent COD's remained about 37 ppm, a precise determination of COD loadings at breakthrough is not possible. Therefore, an estimate was made in September, 1972 as follows:

Feed COD, ppm	Loading Lbs. COD/Lb. Carbon	Carbon Exhaustion Rate Lbs. of Carbon/1,000 Gals. Treated
150	0.35	3
250	0.30	6

This estimate is based on the assumption that the beds are extremely sensitive to surges of COD. The surges may penetrate deep into the bed and prevent the necessary COD removal in the low range. Since rainfall was light, dilution of the COD with rain water was greatly decreased. The result was extremely erratic feed COD concentrations and poor carbon plant operation. It should be emphasized, however, that the estimates are based on assumptions which have not been validated and the estimated loadings have never been achieved prior to breakthrough.

TWO-STAGE TEST RUN

The data in Figure 10 shows that the carbon near the top of the bed adsorbs much more COD than the lower portion of the bed. Therefore, if the bed could be cut in half, only the more heavily loaded top portion would need to be regenerated. This would allow a much higher COD loading. Since an individual cell cannot be split in half, a system was devised to test two cells in series.

Description of System and Operation

Cells number two, six, and seven were used in a two-stage test run from July 12, 1972, through August 30, 1972. Both phases of the downflow upflow system are shown in Figure 19. In order to

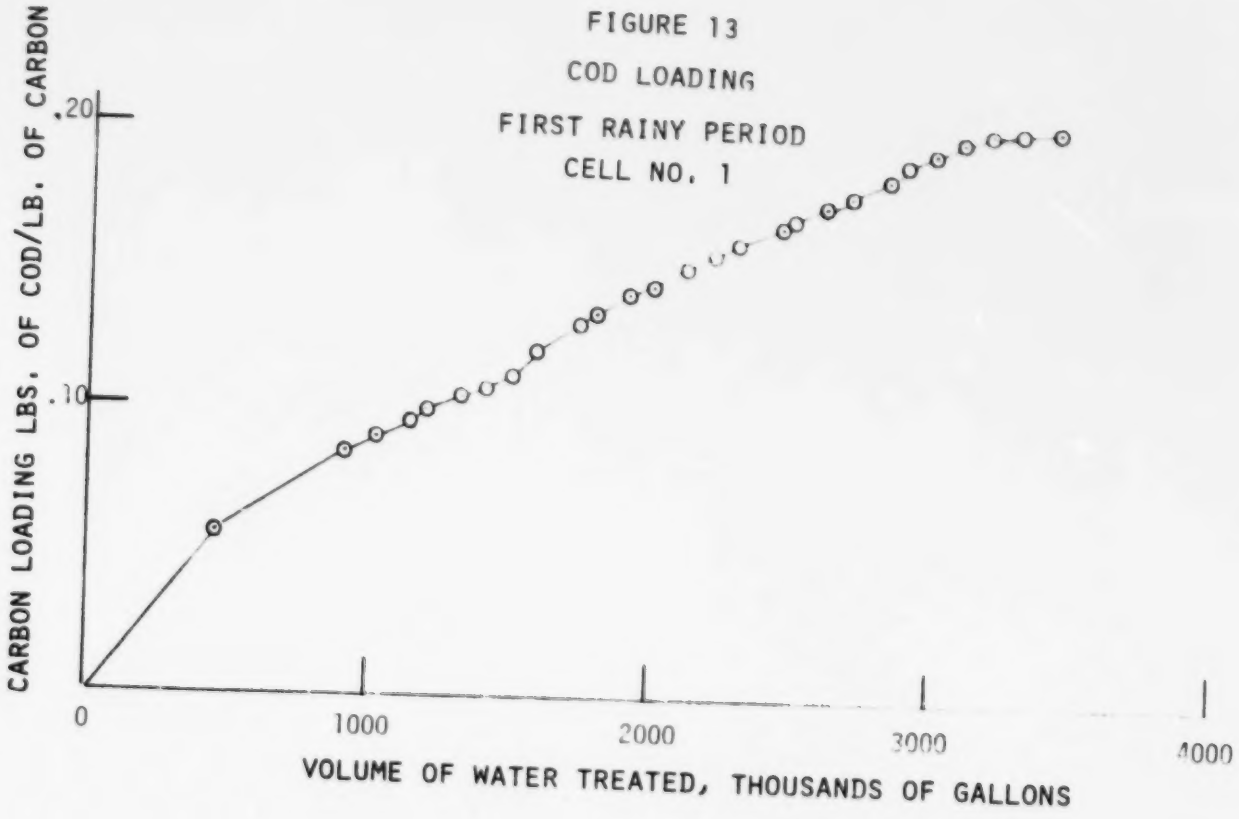

Figure 13. COD Loading First Rainy Period Cell No. 1

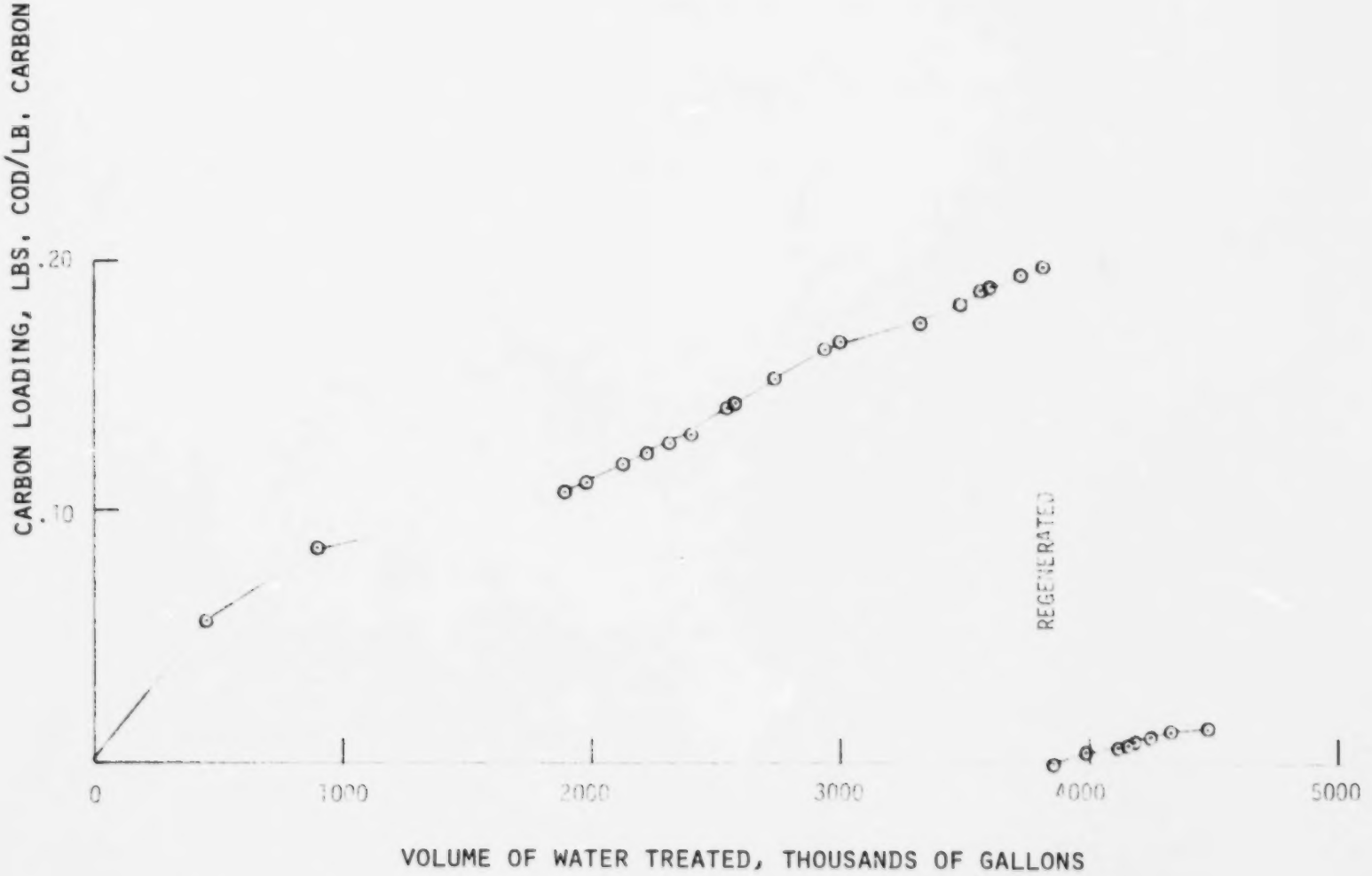

Figure 14. COD Loading First Rainy Period Cell No. 2

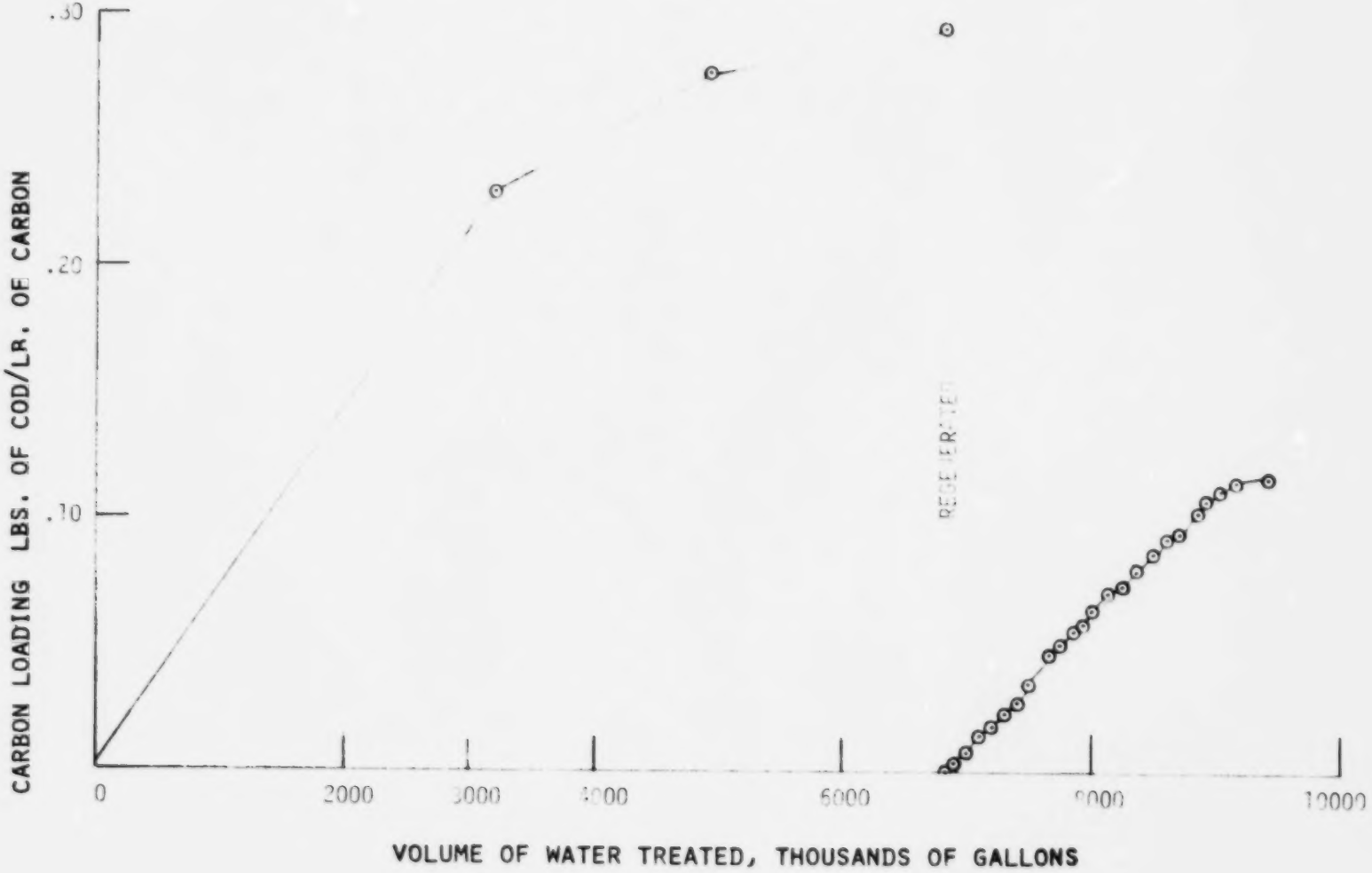

Figure 15. COD Loading First Rainy Period Cell No. 3

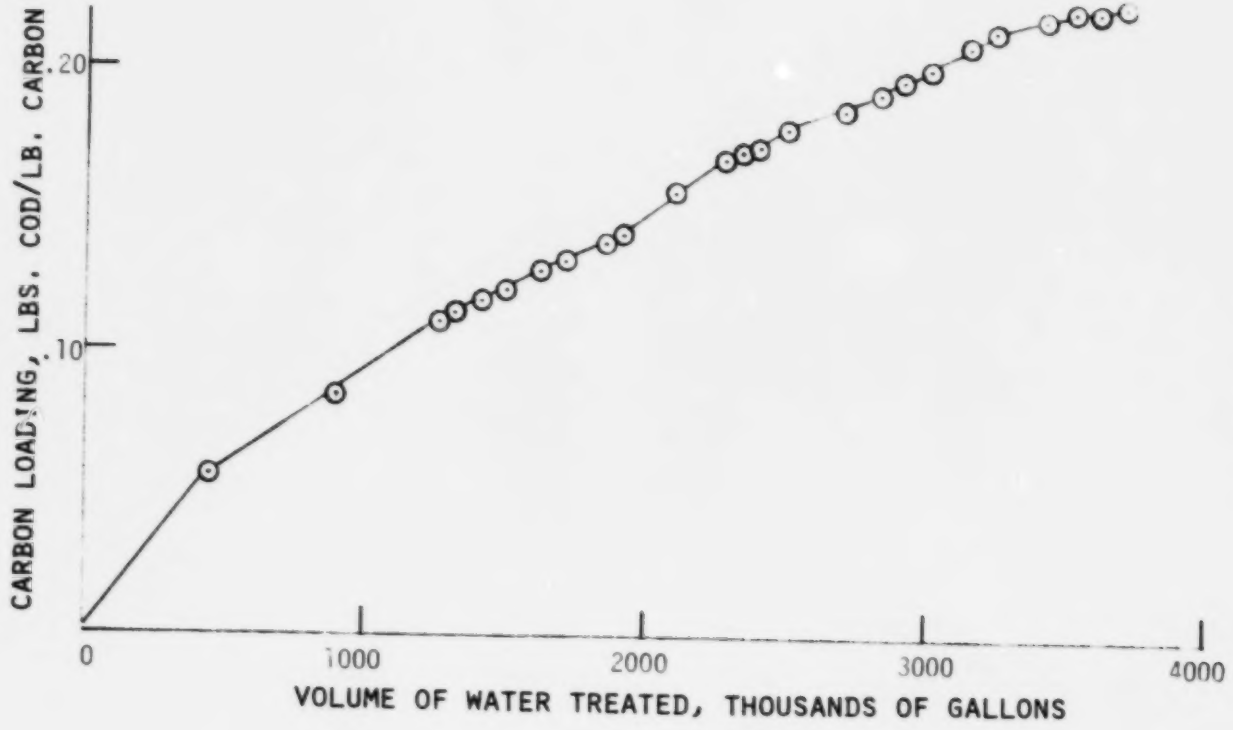

Figure 16. COD Loadings First Rainy Period Cell No. 4

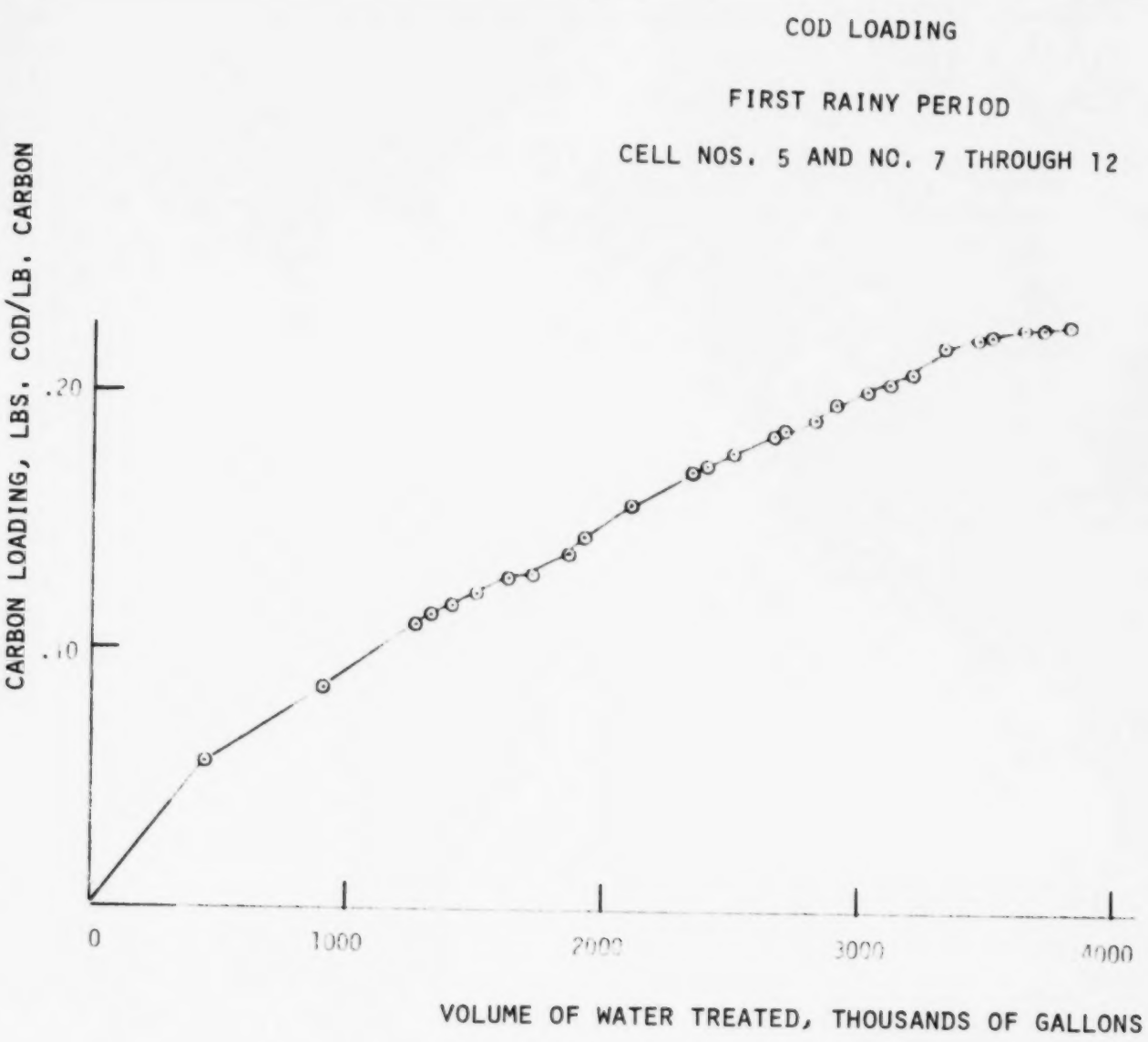

Figure 17. COD Loading First Rainy Period Cell Nos. 5 and No. 7 through 12

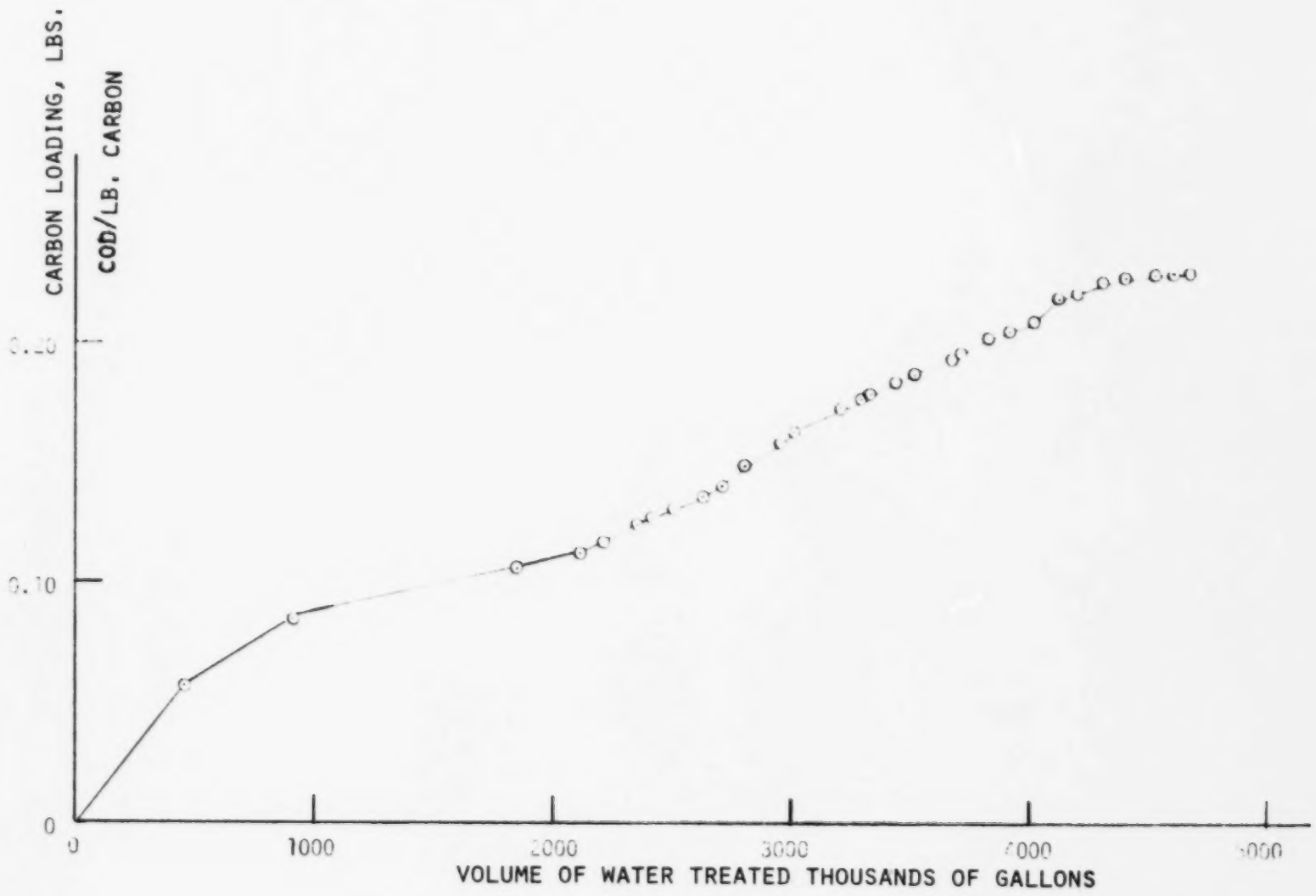

Figure 18. COD Loading First Rainy Period Cell No. 6

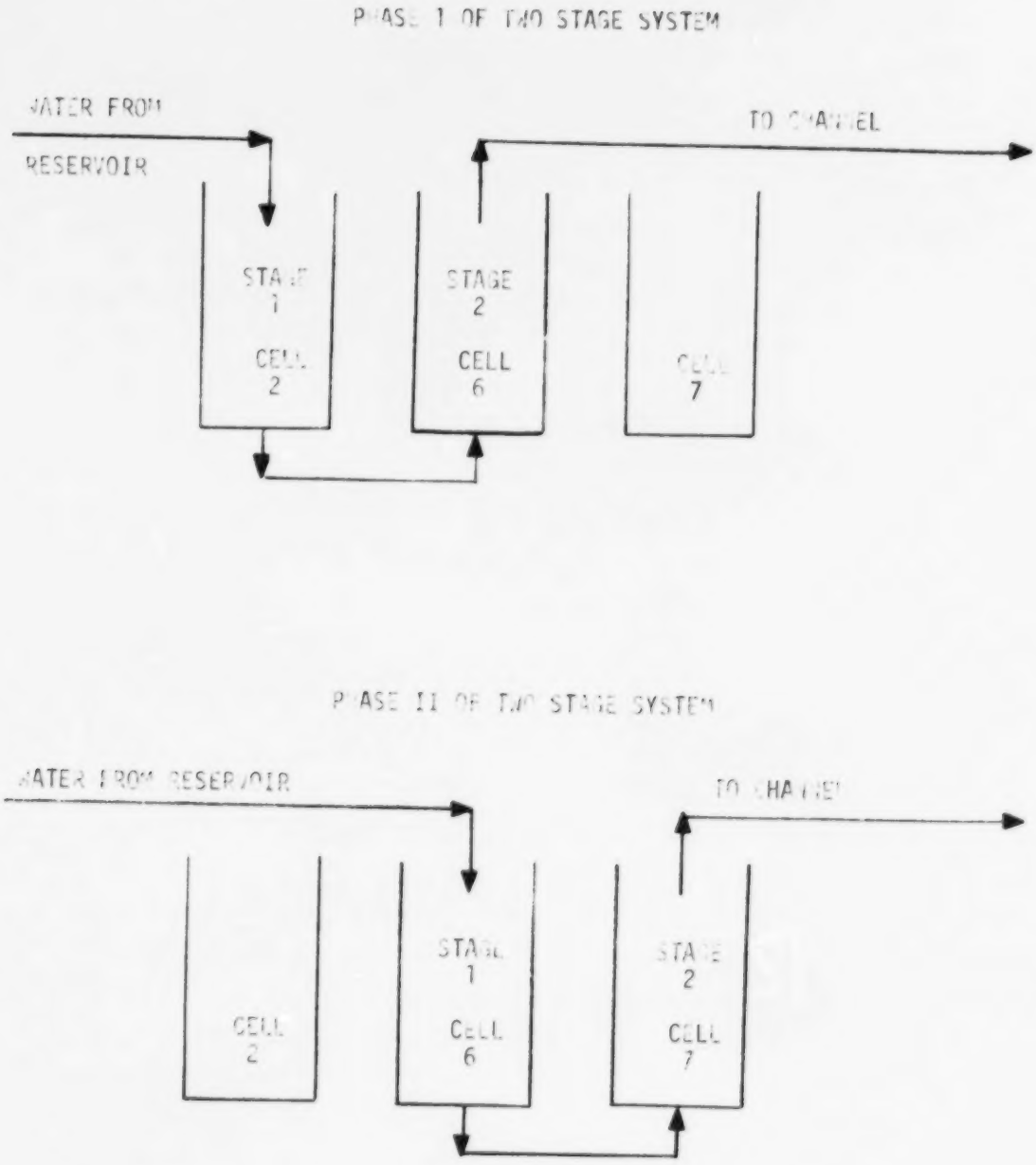

Figure 19. Two Stage System

increase the adsorptive capacity of the unit, 15,000 pounds of carbon were added to the existing 48,700 pounds in each of the cells used. This increased the bed depths from 13 feet to 17 feet to give a total of 63,700 pounds in each cell. The first phase used cell number two as the first stage with downflow, and cell six as the second stage with upflow. At the beginning of the second phase, cell number two was taken out of service, cell number six became stage one with downflow, and cell number seven was placed in service as the second stage with upflow. Since no rain fell during the summer, the feedwater was made up in the impounding reservoir every two or three days using several water sources in an attempt to maintain the COD concentration at 250 ppm.

The feed rate to each cell during the first phase of the test run was held constant at 500 GPM. This is equivalent to the design rate of 3,000 GPM for the entire plant. The feed rate was reduced to 250 GPM for most of the second phase to see if a lower effluent COD could be reached.

Results

The results of the two-stage run are shown in Figures 20 and 21. Figure 20 shows the COD concentrations of the feed, first stage effluent and second stage effluent as a function of gallons of water processed in the unit. Figure 21 shows the COD loading of each cell vs. gallons of water processed. At the end of Phase 1, the first stage had a loading of 0.39 pounds of COD per pound of carbon and the second stage had a loading of 0.11. The effluent COD at the end of Phase 1 was well above the desired 37 ppm. There was also a problem with algae growth, which, as discussed later in this section, was adversely affecting the test run results. Since lower COD effluents were not detected during Phase 2 and because the unit had to be readied for the next rainy season, the run was terminated. As can be seen in Figure 20, the effluent remained below 100 ppm virtually the entire run.

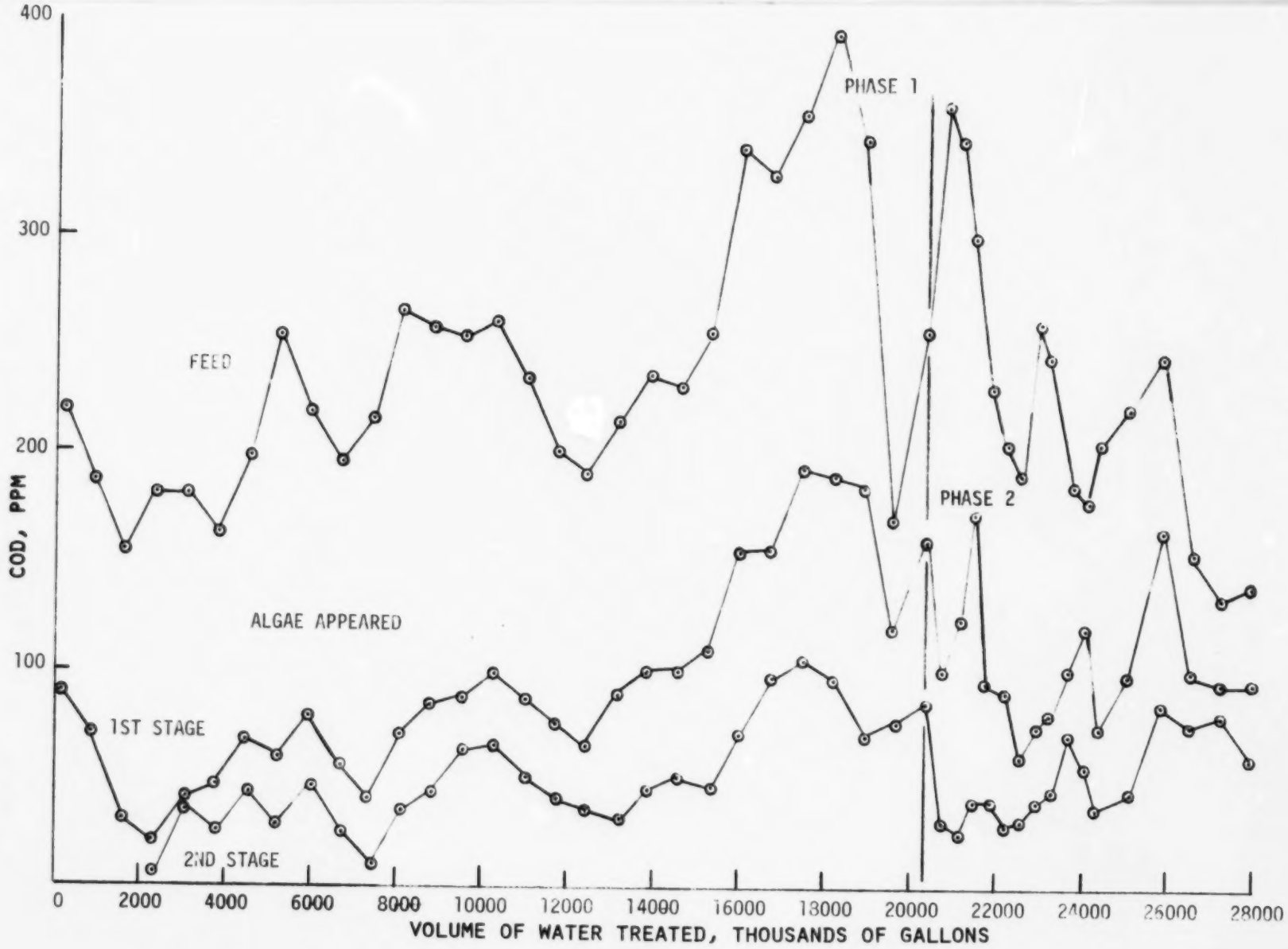

Figure 20. COD Concentrations Two-Stage Test Run

FIGURE 21

CARBON LOADING TWO-STAGE TEST RUN

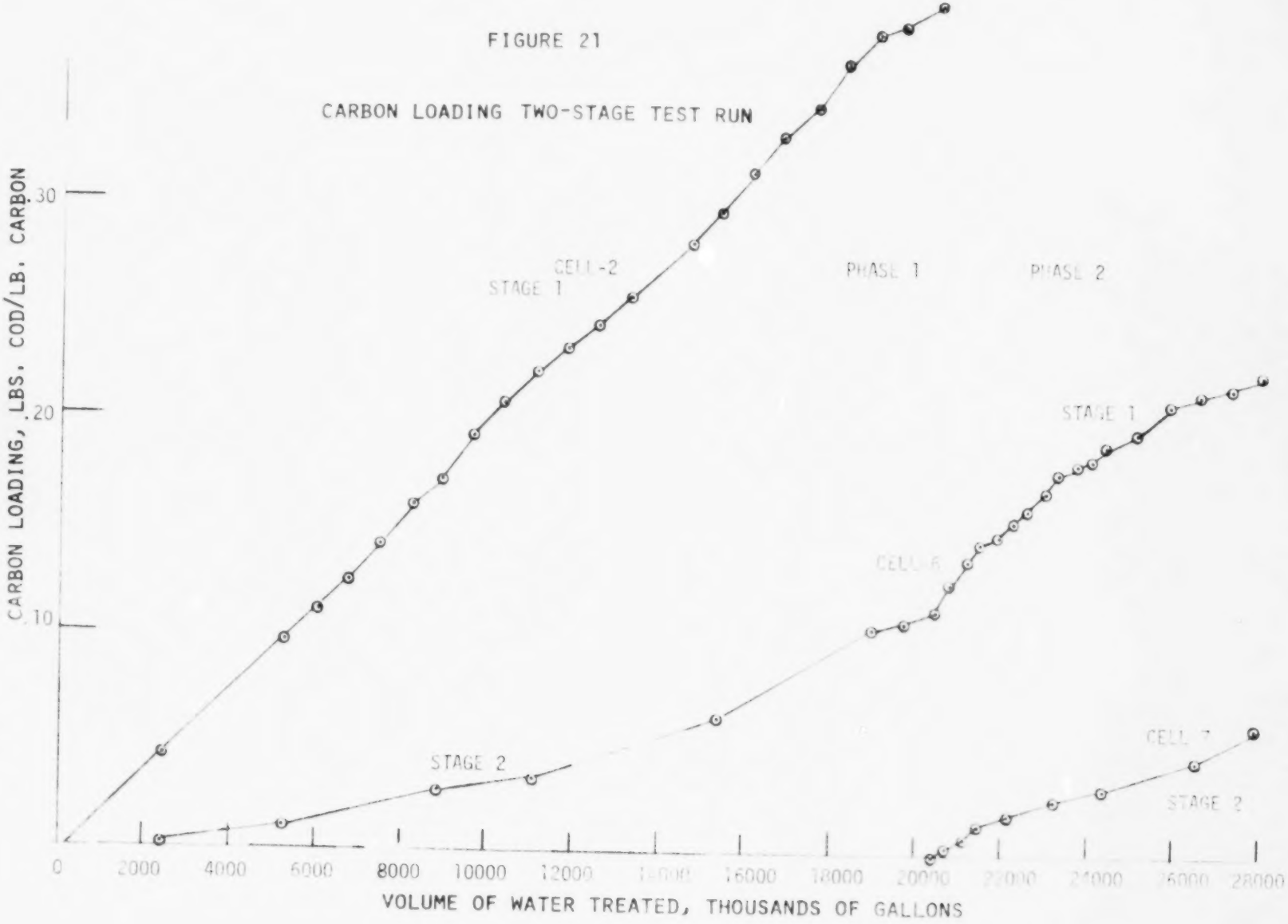

Figure 21. Carbon Loading Two-Stage Test Run

Validity of Results

By the definition used for the Watson Carbon Plant, the carbon is considered loaded when it contains so much COD that its adsorption capability is reduced to the point where it cannot adsorb enough COD to keep the effluent below 37 ppm. Ideally, this loading could be determined by running the carbon plant under the expected rainy season conditions until the effluent becomes greater than 37 ppm, or, in other words, until "breakthrough" occurs. Unfortunately, the system cannot be operated at a steady feed concentration of 250 ppm COD until there is enough rainfall to dilute the COD to 250 ppm. The COD during test runs could not be kept at the desired concentration on a day to day basis because it takes several hours to determine the COD, and thus, any concentration surge would be detected too late. Therefore, an estimate of operation under ideal conditions free of surges and algae was made for the two-stage system as was previously done for the single stage system. This estimate is that the two-stage system can load to 0.39 pounds of COD per pound of carbon. This is the same as attained by the first stage during Phase 1 of the test run.

Algae Growth

Algae growth in the water impounding reservoir first appeared at the end of the first rainy season. The algae was easily identified as it gave the water a green coloration. The carbon adsorption plant was adversely affected by the algae as indicated in run six during the first rains. During this test run, the carbon plant had one of the lowest average feed COD concentrations (147 ppm) tested, and yet, due to the presence of algae, the effluent averaged 93 ppm COD.

The algae problem appeared again in July 18 in the water fed during the two-stage test run. A study of reservoir algae control

revealed that algae growth can be kept low by use of small concentrations of copper sulfate. On July 28, solid copper sulfate was spread over the surface of the reservoir to give a content of about 0.0002 weight percent. Within 72 hours the algae was greatly reduced. Since the effect of the $CuSO_4$ is not permanent and no more addition of $CuSO_4$ was made, the algae became so concentrated that the carbon plant had to be shut down on August 18. Copper sulfate was again spread over the reservoir on August 22 to reduce the algae. Three days later it was added again which kept the algae at low levels until the end of the two stage test run.

Since the algae problem was never experienced again, no further investigation was made into its control.

Evaluation of Two-Stage System

The one-stage system can load to an estimated 0.30 while the two-stage system can load to an estimated 0.39. This gives the two-stage system a distinct advantage over the previous single stage operation. The two-stage system also has the advantage that it ran longer than any test run and had one of the lowest average effluent COD concentrations (47 ppm). It should be re-emphasized, however, that the predicted loadings of the carbon used for comparison have never actually been achieved prior to breakthrough.

SECOND RAINY PERIOD

Single Stage System

Although plans called for converting the carbon plant to a two-stage system if it proved superior, a change in Los Angeles County sanitation regulations allowed rain diluted waste water to be pumped to the sewer. Previously, only limited quantities of impounded water were permitted, and then only if COD was above 450 ppm. The plant was used as a single stage system to process impounded water from October 1972, through July 1973, since pumping limitations prevented discharging all impounded water to the sewer.

The 12 carbon cells were divided into two groups: (1) those for testing purposes; and (2) those for handling the bulk rain water. To allow the accumulation of additional data under controlled conditions relative to alternative modes of operation, five of the cells were designated for use only for testing purpose. The remaining seven were designated for use in processing the bulk rain water as it was impounded.

Staggered Mode Operation Test Run

The choice of five cells for test purposes is based on the calculations shown in Table 3. These calculations were used to estimate the maximum number of cells which could be operated continulusly based on predicted plant limitations. The calculation is simply a determination of how much water can be processed to load carbon at the same rate it can be regenerated. A staggered operation was devised to allow three cells to operate at all times without delay for regeneration. In order to start the test run, it was necessary to start one cell each week. At the end of three weeks, a fourth cell was started while the first cell was moved to the spent carbon tank and regenerated. At the end of the fourth week, the first cell had been regenerated and was ready for use. However, a fifth cell was used and the first was put on stand-by to be used at the end of the fifth week. The extra fifth cell was used as a buffer against temporary mechanical holdups. The mode of operation is shown in Figure 22.

Since the impounding reservoir had a high COD content, effluent water was recycled back to dilute the feed as is shown in Figure 23. The total feed rate to each cell, which includes the recycle was maintained at 250 GPM while the unit was in operation. Air was dispersed into the effluent sump to kill anerobic bacteria that might be recycled to the beds.

Table 3. ESTIMATE OF MAXIMUM WATER THROUGHPUT

Estimated Feed COD	300 ppm
Estimated Loading	.30 Lb. COD/Lb. Carbon
Estimated Carbon Regeneration Ability	9,000 Lb. Carbon/Day
Estimated Effluent COD	30 ppm

$$8.34 \times 10^{-6} \frac{\text{Lb. COD}}{(\text{Gal. } H_2O)(\text{ppm COD})} \cdot (300 \text{ ppm} - 30 \text{ ppm}) = 2.252 \times 10^{-10} \frac{\text{Lb. COD}}{(\text{Gal. } H_2O)}$$

9,000 Lb. Carbon/Day (.30 Lb. COD/Lb. Carbon) = 2,700 Lb. COD/Day

$$\frac{2{,}700 \text{ Lb. COD/Day}}{2.252 \times 10^{-3} \text{ Lb. COD/(Gal. } H_2O)} \frac{1}{24} \text{ Hrs./D} \frac{1}{60} \text{ M/Hrs.} = \underline{833 \text{ GPM}}$$

With a feed rate to each cell of 250 gpm, 3 cells were used for a total of 750 gpm.

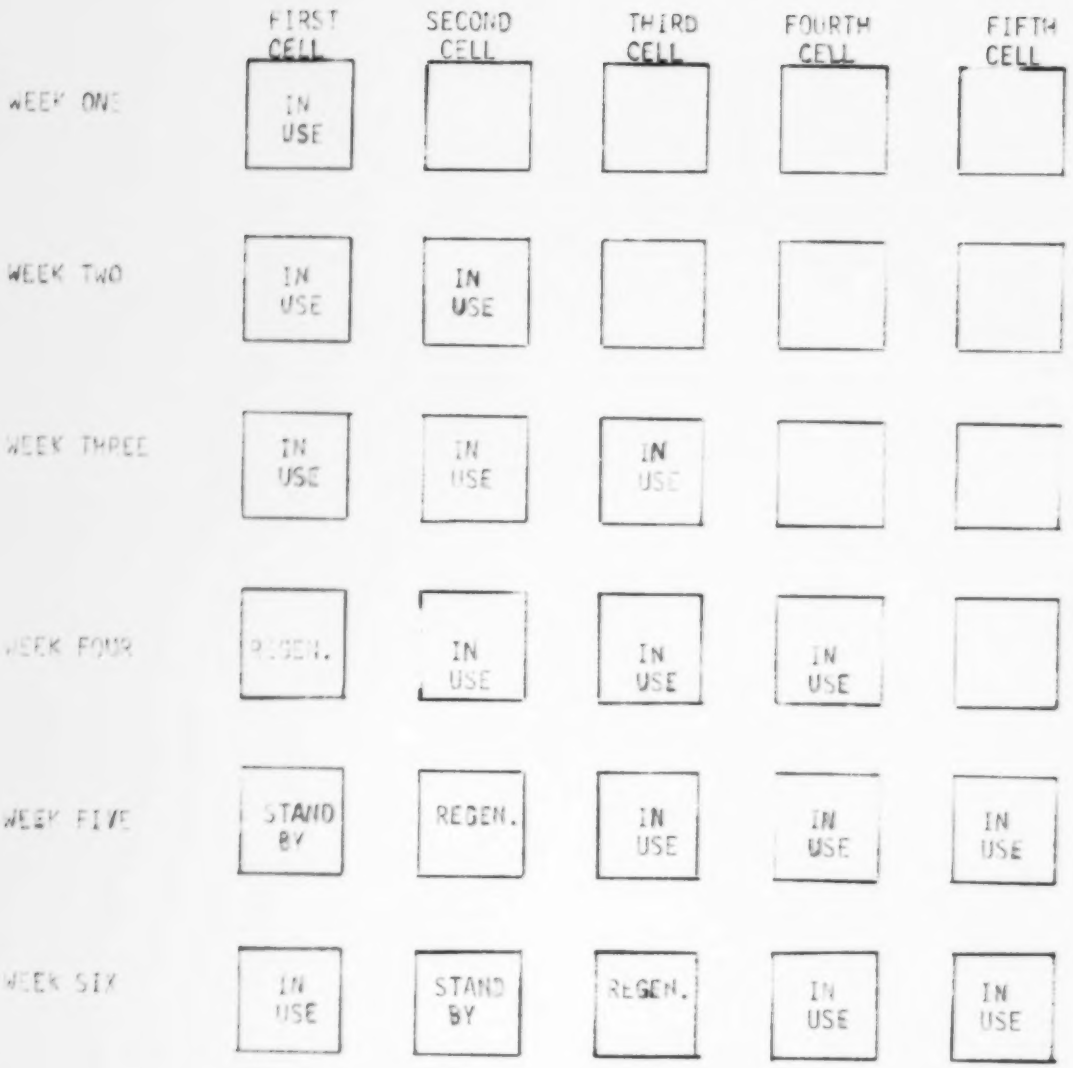

Figure 22. Five-Cell Staggered Operation Test Run

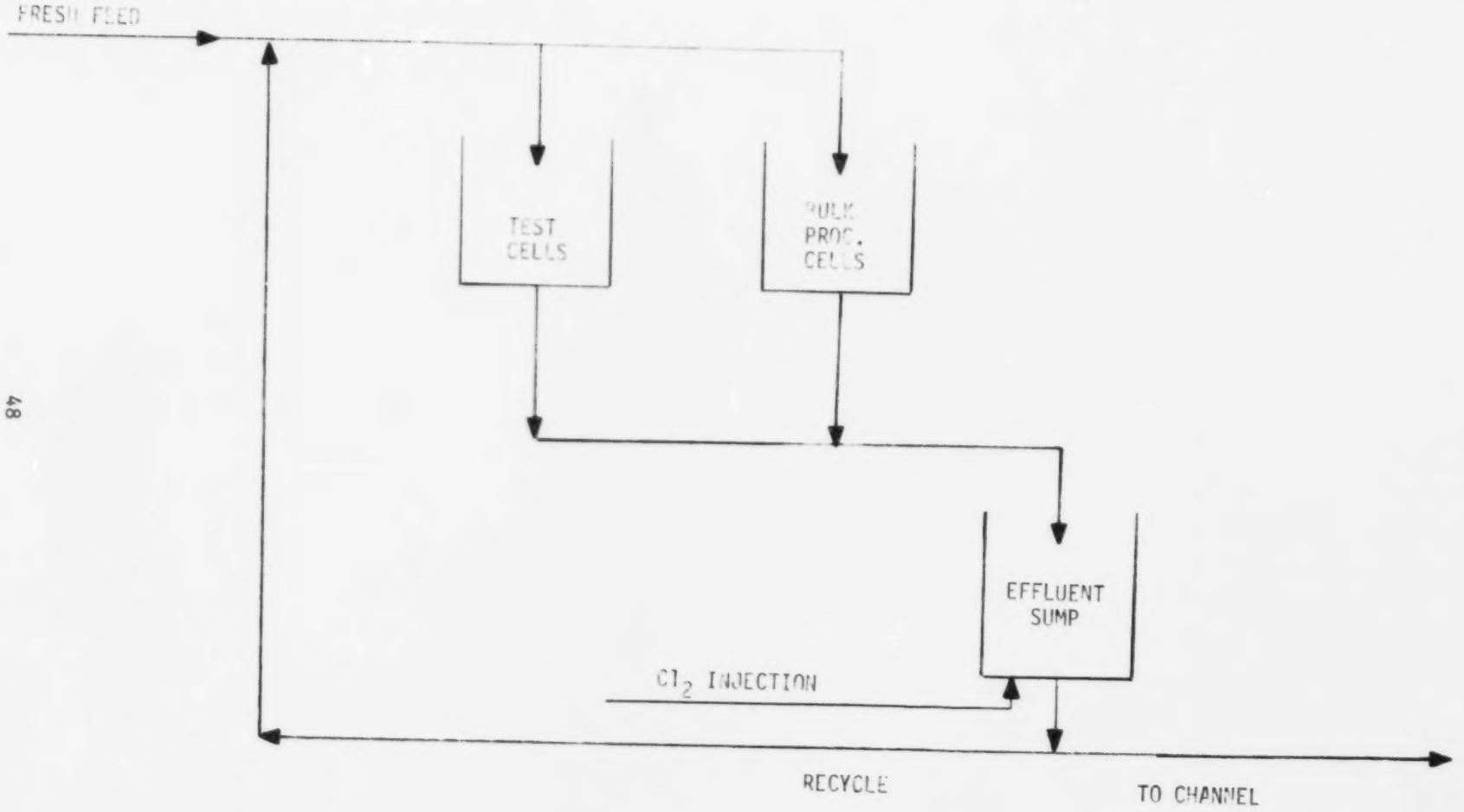

Figure 23. Secondary Rains Recycle Operation

The COD concentrations and loadings of each of the five cells are plotted in Figures 24 through 28.

After the cells had finished one cycle, it was apparent that the carbon could not keep the effluent COD below the desired 37 ppm for a full week, despite the dilution of the feed. Therefore, it was decided to chlorinate the effluent in the hope that COD molecules which had not been adsorbed on their first pass through the bed might form a halogenated molecule which would be more likely to be adsorbed. The chlorine was added at 100 pounds per day for the remainder of the test. Since it was difficult to determine the effects of the chlorine addition, the cells were not switched as scheduled. They were run an extra two weeks before it was decided that there were no noticeable improvements with the chlorine.

Processing Bulk Rain Water

Seven of the 12 cells were used for processing bulk rain water during the second rainy season. Bulk rain water refers to water in the reservoir when the level in the reservoir is high enough to limit the ability to impound water beyond reasonable expectations.

About 40.6 million gallons of water were processed through the seven cells. The influent and effluent COD's along with the carbon loading are plotted vs. gallons of total water treated in Figure 29. The chlorine addition start time is also indicated in Figure 29. When the rain season ended, the cells were loaded to 0.31 pounds of COD per pound of carbon.

Evaluation of Second Rainy Period

During the second rainy period 102,000,000 gallons of water were processed. The average diluted feed COD concentration was 233 ppm while the effluent averaged 48 ppm with a high of 95 ppm. The carbon loaded to an average of 0.26 pounds of COD per pound of carbon.

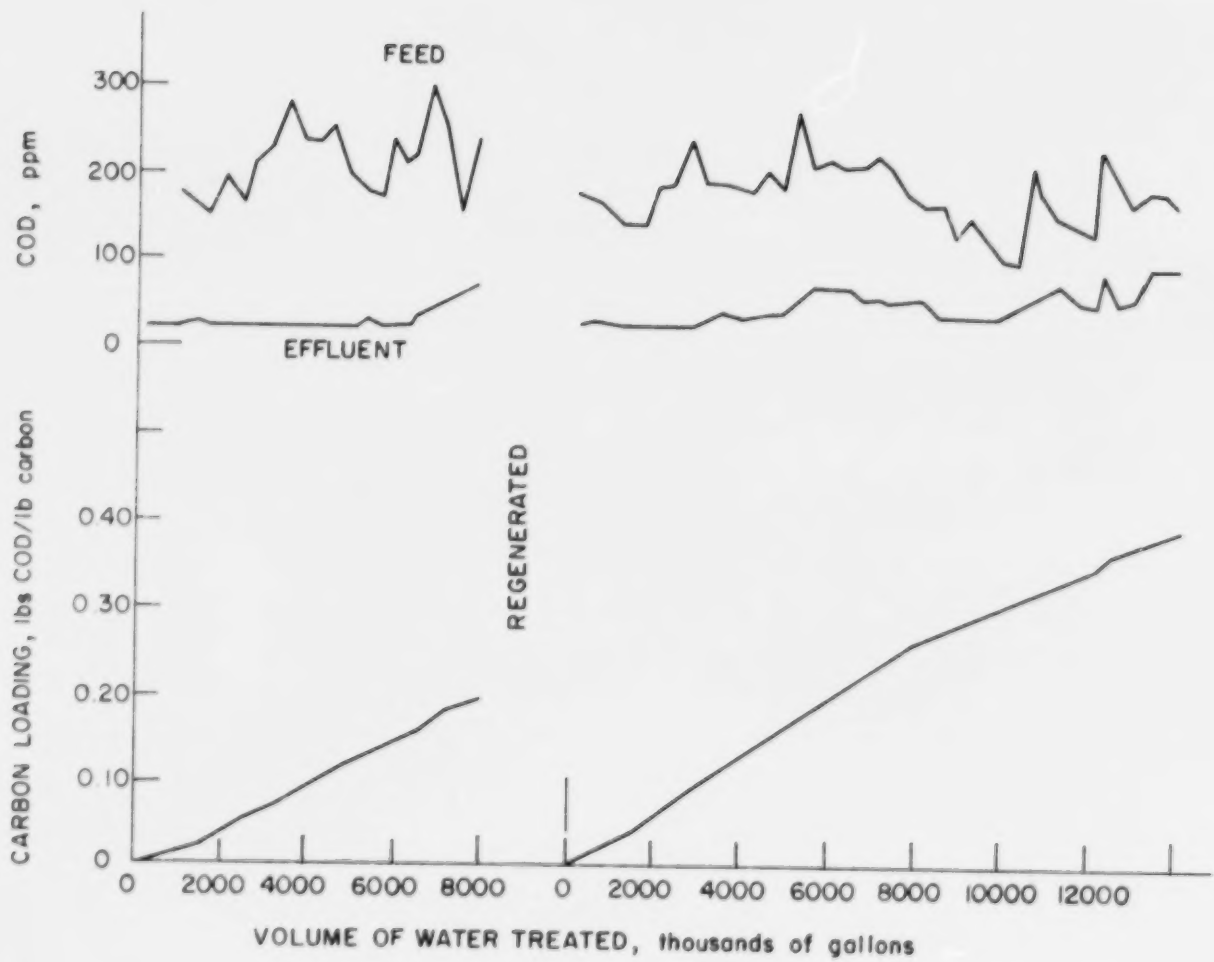

Figure 24. Adsorption Data Second Rains
Cell 1

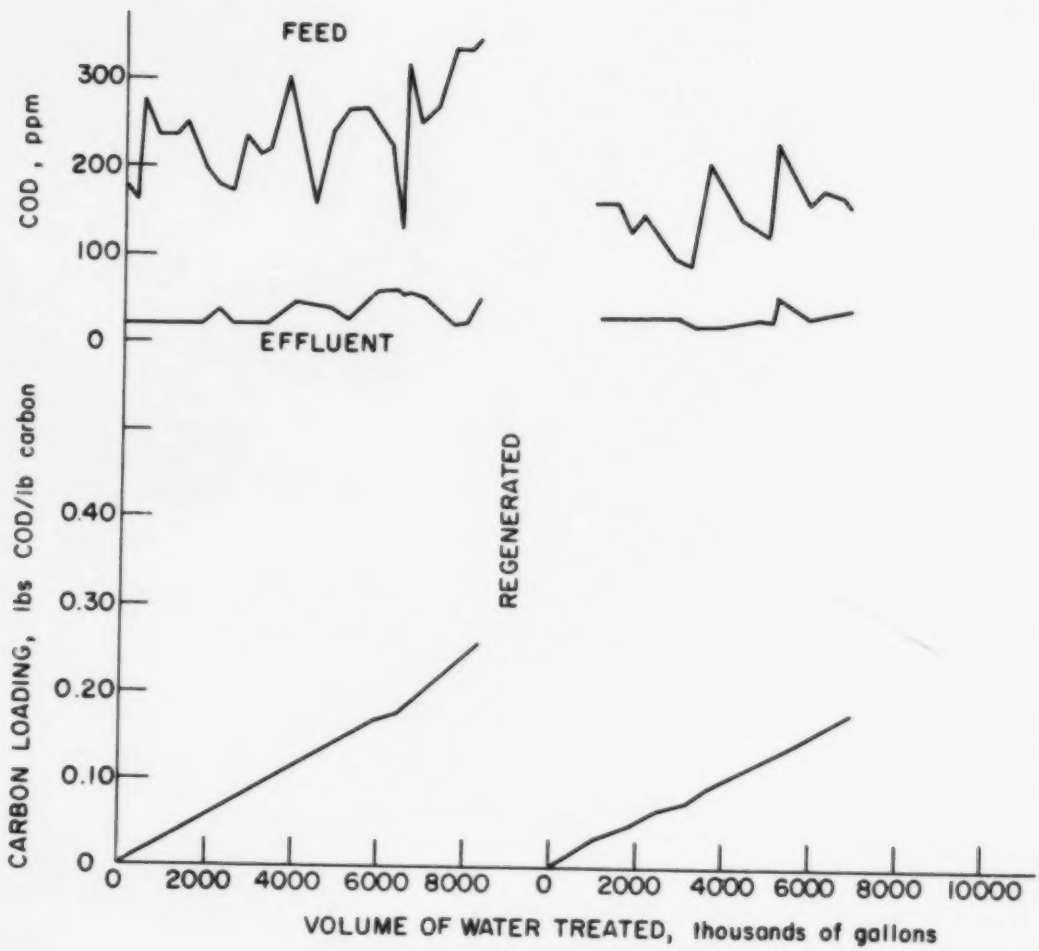

Figure 25. Adsorption Data Second Rains
Cell 3

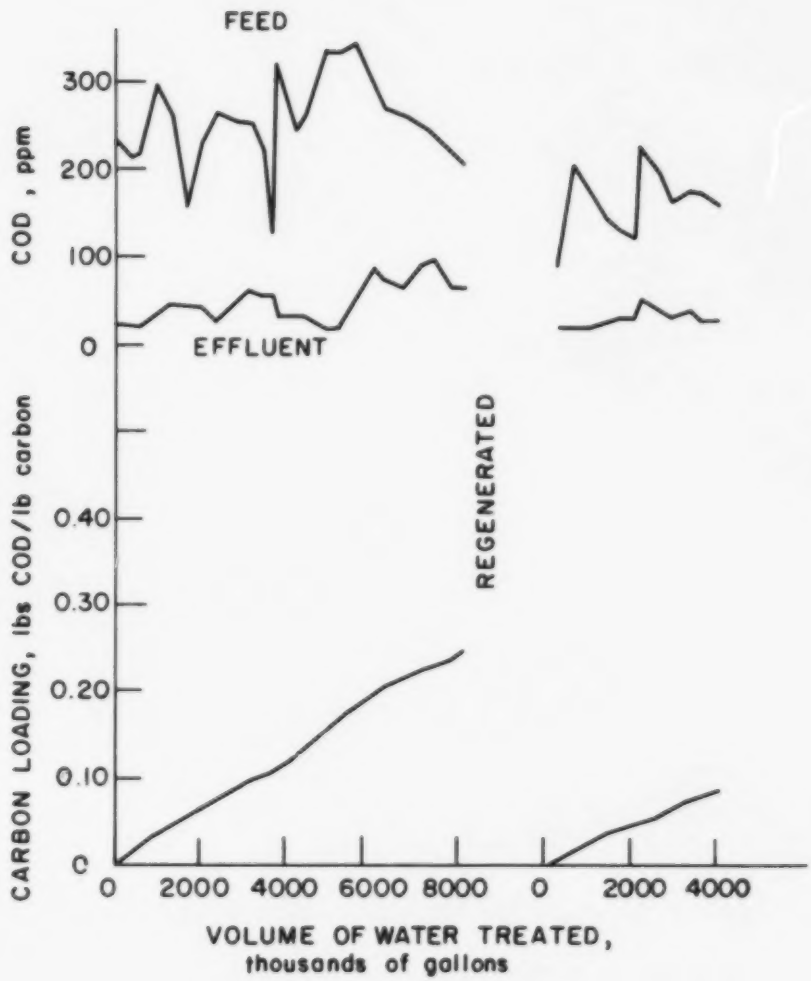

Figure 26. Adsorption Data Second Rains
Cell 5

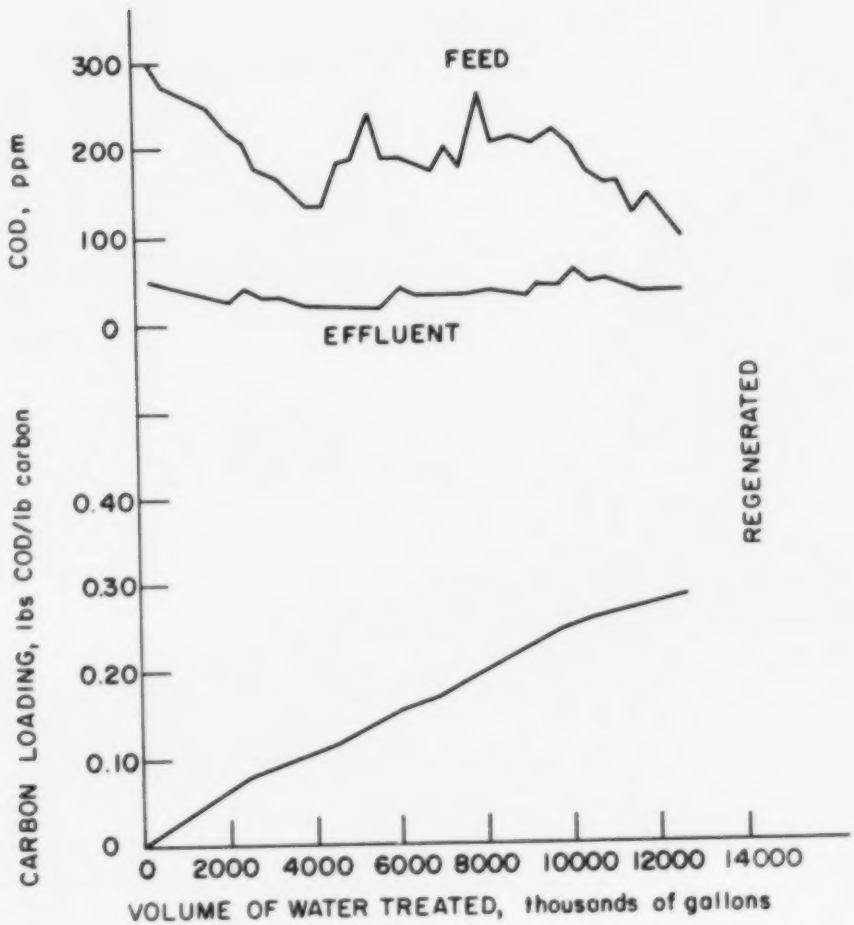

Figure 27. Adsorption Data Second Rains Cell 7

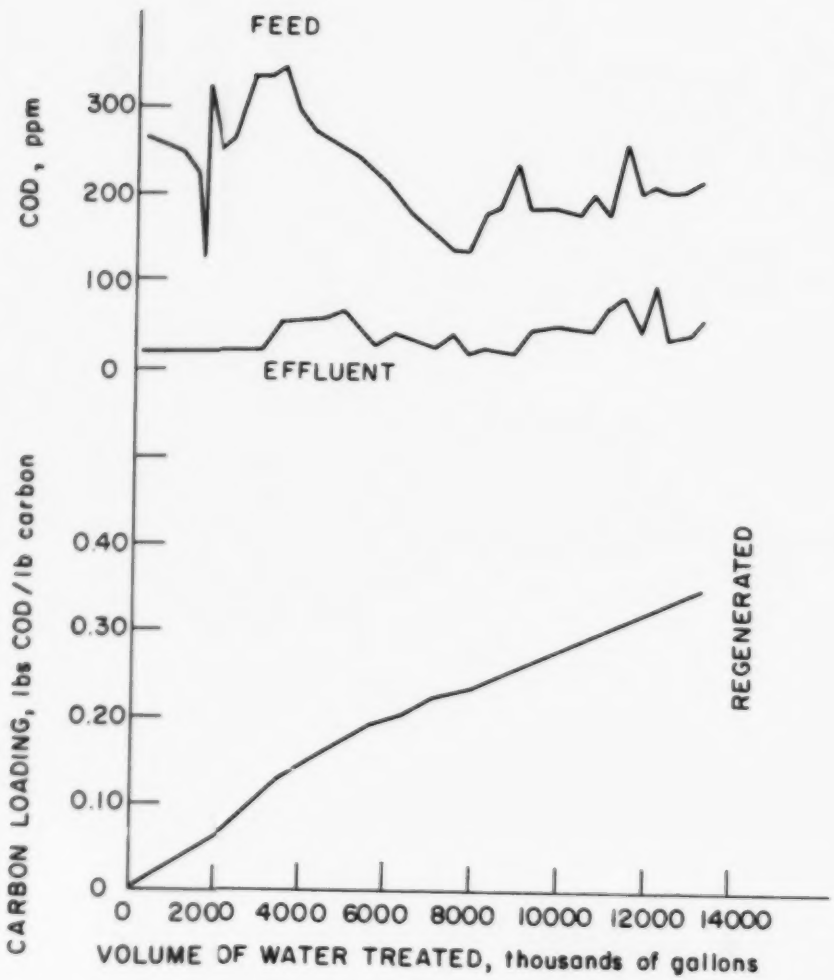

Figure 28. Adsorption Data Second Rains Cell 9

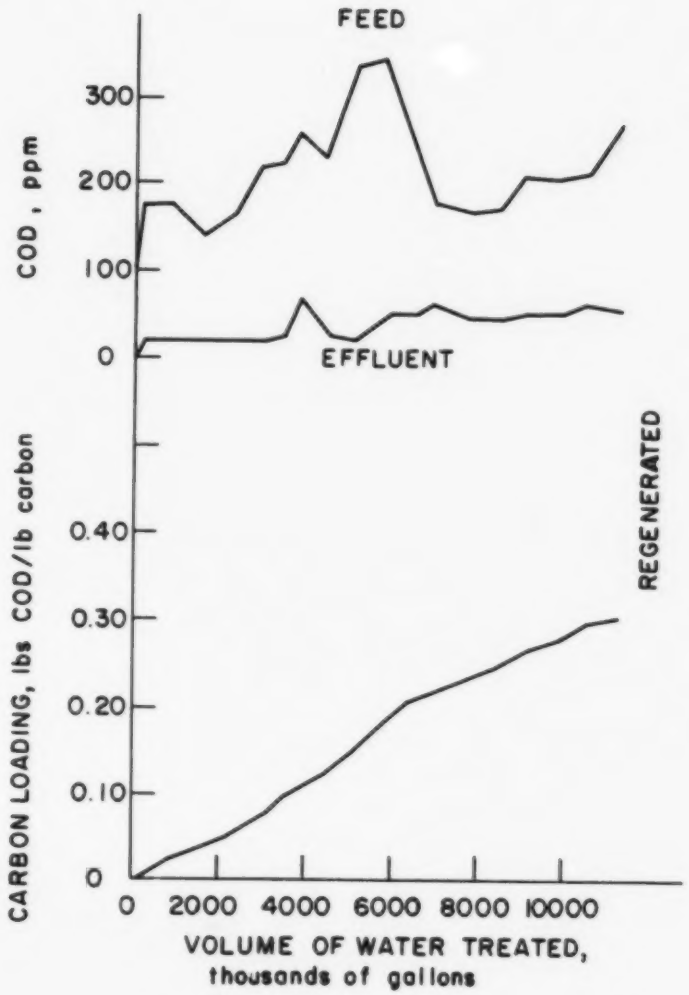

Figure 29. Adsorption Data Second Rains
Cell Nos. 2,4,6,8,10,12,11

Although the carbon plant was operated without violating the limit of 1330 pounds per day of COD, a large portion of the impounded water was not processed in the plant. The change in county regulations relieved the need for meeting design operation. The controlled COD level in the feed allowed for the highest average carbon loading during the two-year project.

The five-cell test run showed that control of the feed COD concentration improves carbon loading.

SECTION VIII

OPERATION AND EVALUATION OF REGENERATION FACILITIES

This section of the report covers the operation of the carbon regeneration furnace and carbon transfer equipment.

FIRST PERIOD OF OPERATION

Twelve cells were regenerated during the first period of operation. The time required for regeneration for the first seven cells is tabulated in Table 4. The time includes all downtime for repairs. The regenerations vary in time from 4.0 days to 14 days with an average of 9.8 days. The unit was designed to regenerate a bed in 5.7 days. The causes of the extended regeneration time are discussed below.

Temperature Excursions

During the first regenerations the temperature on hearths four and six would fluctuate from 1700°F to 1850°F in 10 to 20 minute cycles. Several attempts were made to adjust the controllers but there was no improvement. The thermowells were changed from 3/4" standard wall to 1" heavy wall stainless steel and the thermocouples were changed from iron constintan to chrome alumal. The temperature controller on hearth six was found in need of repairs and was fixed. The temperature excursions were reduced to only 50°F in future runs.

Eductor Wear

The original design used 1" cast iron eductors and 110 pound per square inch motive water to transport carbon to the furnace screw

Table 4. TIME REQUIRED FOR REGENERATION

CELL NO.	START	FINISH	TIME REQUIRED hours	days
3	9 AM, Nov. 2, 1971	10 PM, Nov. 10, 1971	205	8.5
2	2 PM, Feb. 17, 1972	4 AM, March 1, 1972	302	12.6
6	9 AM, April 19, 1972	6 PM, April 27, 1972	201	8.4
8	4 PM, May 11, 1972	10 PM, May 20, 1972	222	9.3
10	3 PM, May 26, 1972	3 PM, June 9, 1972	336	14.0
12	2 PM, June 12, 1972	12 N, June 17, 1972	118	4.9
11	1 AM, June 20, 1972	3 PM, June 30, 1972	254	10.6
		Total	1638	68.3
		Average	234	9.8

feeder and away from the furnace regenerated carbon quench tank. The capacity of these eductors when in new condition was about 6.5 pounds of carbon per minute. Due to erosion of the throat, both of the eductors lost efficiency after three regenerations. This loss of efficiency limited the feed to the furnace. In addition to the eductors wearing out, they had many problems with plugging, but this was alleviated with screens to stop large chunks from entering the eductors.

High Gas Velocities

A problem with fines blowing out the stack was encountered, but was alleviated by lowering the steam rate.

High Shaft Rates

Due to mechanical problems, the shaft which moves the rabble arms over the carbon was rotating at three RPM instead of the design rate of 1 RPM. The rate was reduced to two RPM's after adjustments were made. During the seventh regeneration, the bolt which locks the motor drive shaft to the drive gear broke. This may have been due to running the rabble arms above design rate.

Evaluation of Furnace Problems During the First Period of Operation

Most of the problems encountered with the furnace operation were mechanical in nature. Therefore, they could be solved as more experience was obtained.

TWO-STAGE TEST PERIOD

Operation

The three cells used in the two-stage test run were regenerated without stoppage for mechanical problems. The major reason for the success was larger eductors and reduced motive water pressure. The 1" cast iron eductors were replaced with 1 1/2" stainless steel eductors. The changes allowed the carbon to be moved without wear or plugging. The uninterrupted feed of carbon allowed for a steady operation and the temperature excursion problem ceased to exist. The new eductors allowed the flow of carbon to go as high as 10 pounds per minute. The data from the regeneration is given in Table 5. Figure 30 shows a plot of regenerated carbon relative efficiency vs. carbon feed rate to the regenerator.

Evaluation of Improved Regeneration

The larger eductor is believed to have solved most of the regenerator problems.

Figure 30 is based on limited data, and thus, the accuracy is questionable. However, the general trend of decreased quality of regenerated carbon with increased feed rate is believed correct.

Table 5. DATA FROM CARBON REGENERATION

DATE	CARBON FEED RATE pounds/min.	APPARENT DENSITY SPENT	APPARENT DENSITY REGEN.	RELATIVE EFFICIENCY SPENT	RELATIVE EFFICIENCY REGEN.
September 18		.59	.495		
19		.58	.52		
20	6-6.5	.58	.515		95.8%
21			.49		94.3%
22	7-7.5		.48		88.0%
23	8-8.5		.48		88.0%
24		.52	.475	64.6%	79.7%
25	10		.465		86.5%
26		.55	.48	27.6%	86.5%
27		.55	.46	67.7%	85.9%

SECOND RAINY PERIOD

During the second rainy period, regenerations continued with no problems. A major portion of the time was spent collecting data for improving testing techniques which are discussed in detail in the "Test Methods and Their Evaluation" section of this report.

On April 23, 1973, the APCD tested the regenerator furnace stack for CO and found the CO content over the allowable concentration of 0.2% by volume. This forced a shutdown of the furnace. It was felt that the insufficient combustion efficiency was caused by the combustion air damper set nearly closed and a low afterburner temperature.

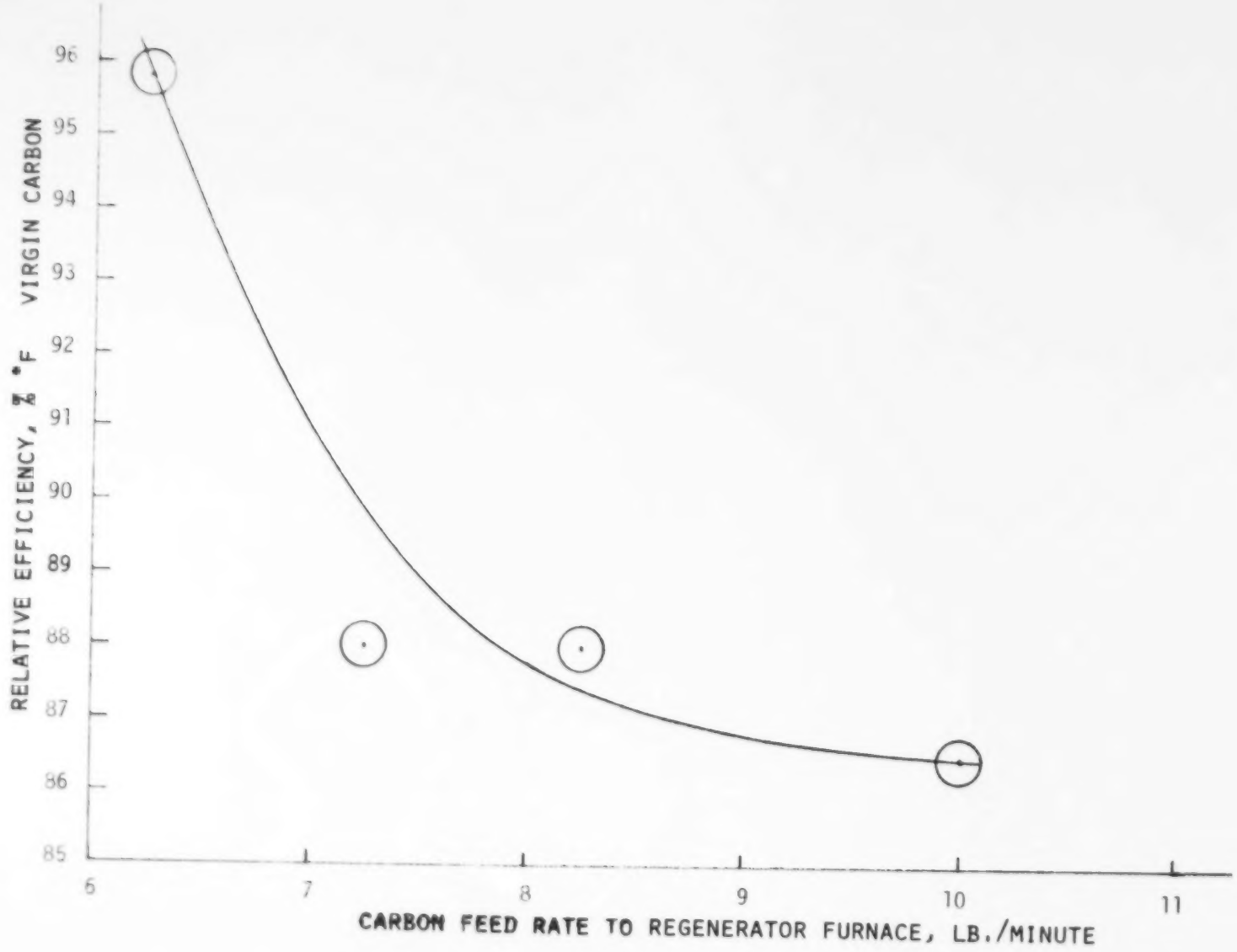

Figure 30. Furnace Operation

Upon obtaining a test permit the furnace was restarted in October 1973, with the combustion air damper wide open and the temperature controller increased from 1400°F to 1550°F. With these changes the CO is well below pollution concentration.

SECTION IX

TEST METHODS AND THEIR EVALUATION

COD DETERMINATION

There are several means of determining the chemical oxygen demand (COD) of a solution. Three of these methods, which are described in Appendix A are EPA HIGH LEVEL method (STORET No. 00340), EPA LOW LEVEL method (STORET No. 00335), and the AquaRator method.

The criteria considered in deciding which method to use for COD determination were time necessary to obtain results, accuracy, and acceptability of results. Both EPA methods are well established but are time consuming. The AquaRator, on the other hand is extremely new and yields results in minutes. A series of tests were run using two types of standard solutions to determine the accuracy of each of these methods. The results are given in Table 6.

The high level method was selected because it is widely accepted and because it covers the required range of COD's. It has a major drawback, however, because it takes about four hours to obtain results. The low level method was not used because of its limited range, and because it was not felt to have any superior accuracy when compared to the other methods in the 30 to 50 ppm COD range.

The usefulness of the AquaRator was the subject of continuous discussion. Results could be obtained in about 20 minutes. At times the device would yield reproducible and fairly accurate

Table 6. ACCURACY OF COD TESTING PROCEDURES
mg/l

STANDARD SOLUTION RUN NUMBER	EPA HIGH LEVEL COD METHOD STORET NO. 00340						EPA LOW LEVEL COD METHOD STORET NO. 00335						AQUARATOR COD METHOD		
	SUCROSE			SODIUM ACETATE			SUCROSE			SODIUM ACETATE			SUCROSE*		
	1	2	3	1	2	3	1	2	3	1	2	3	1	2	3
COD STANDARDS mg/liter															
10	15	14	14	10	12	12	18	12	14	11	9	8	13	12	12
30	32	28	32	26	26	21	35	36	32	31	31	32	29	30	31
50	52	48	54	44	44	52	55	57	57	46	46	46	45	44	46
120	124	125	123	106	107	108							116	117	118
250	266	267	261	240	230	227							221	215	223
500	551	549	551	484	478	476							423	428	423

* For AquaRator, sodium acetate solutions were used as standards.

results, while at other times it yielded erratic results. Due to these problems, it was not felt that the AquaRator could be used for determining effluent COD's despite the speed of obtaining results. The AquaRator was used during the second rainy period to aid in determining recycle rate. Because of the need to keep net feed level at about 250 ppm COD, up to date results were required. The EPA method was too time consuming to be used as a control aid.

Another subject of concern was the identification of COD materials. COD is referred to in this report as if it were a known, identifiable substance, but actually it is a wide variety of materials which can consume dissolved oxygen. These materials can vary in size from several atoms to large complicated molecules and can be organic or inorganic. When these various materials are adsorbed onto activated carbon they will all affect the loading of the carbon in different ways. For this reason, it would be of value to know what materials make up the COD in the feed and effluent streams. With a knowledge of what is adsorbed and what is not adsorbed, improvements in operations might be made.

An attempt was made to identify the COD materials, but due to the small amounts and difficulty of analyzing hydrocarbons and water mixtures, very limited results were obtained. These results were obtained by the United States Environmental Protection Agency's Petroleum-Organic Chemicals Wastes Section, Treatment and Control Technology Branch and are given in Appendix C. These findings indicated the organic compounds in the effluent have a higher percentage of higher molecular weight compounds than the feed.

More work is needed in the area before a true understanding COD adsorption onto activated carbon can be attained.

REGENERATED CARBON TEST METHODS

A major effort was put forth during the two-year project to find a reliable means to determine the quality of regenerated carbon. The major reason for the study was to give operating personnel a target for furnace operation.

Two tests which were run on a regular basis during regenerations are the apparent bulk density (ABD) test and the relative efficiency (RE) test. These test methods are described in detail in Appendix B. The apparent bulk density test takes about two minutes to run and is simply a quick determination of unpacked density of the carbon. The relative efficiency test is a time consuming comparison of the adsorptive capacity of carbon sample with virgin carbon.

The criteria considered in selecting which test method to use as an operational tool for the regenerator furnace were time required, accuracy, and reliability of results. During regenerations, operating personnel have relied on the ABD test simply because it can be run on site in a couple of minutes. If the delta ABD between spent and regenerated carbon changes significantly from 0.06 gr/cc, the operating personnel alter the burning rate. The RE tests take several hours to run and are, therefore, not used as an operational tool. The RE tests do, however, allow a more direct comparison of adsorptive ability compared to virgin carbon. The mode of operation used has resulted in carbon of essentially constant quality based on RE tests within the limits of the determinations Representative ABD, Delta ABD, and RE data are given in Table 7.

Since, as described previously in this section, there are many types of COD material with different adsorption characteristics, it was decided to use process water instead of sucrose as a standard for the RE test. This was done in the hope that the process water would be more likely to be adsorbed in a similar matter as

Table 7. COMPARISON OF ABD AND RE TESTS

Date	Regenerated ABD	Delta ABD	Relative Efficiency
First Rains Regenerations			
11/3/71	0.531	--	66%
11-5-71	0.504	0.07	59%
11-6-71	0.587	--	69%
11-7-71	0.499	--	72%
11-9-71	0.499	--	83%
11-10-71	0.493	--	82%
Second Rains Regenerations*			
3-3-73	0.50	0.05	102
3-9-73	0.49	0.06	102
3-10-73	0.50	0.06	102
3-13-73	0.49	0.07	101
3-15-73	0.50	0.07	98
3-17-73	0.47	0.07	98
3-24-73	0.48	0.05	98

*Further data is given in Table 8 for the second rains regeneration.

the carbon plant feed. The results of the RE tests using the two standards are compared in Table 8. The RE tests using processs water give erratic results. This is believed to be due to the fact that the process water used for the tests is obtained on different days and thus is not a good standard.

Therefore, even though the sucrose RE test is not necessarily representative of how COD material will adsorb, it appears to be a better test for comparing regenerated carbons.

TABLE 3

COMPARISON OF RELATIVE EFFICIENCY TESTS

FOR REGENERATED CARBON

DATE	ABD	RE USING SUCROSE	RE USING PROCESS WATER
1-19-73	0.44	98	101
1-20-73	0.41	99	103
1-21-73	0.44	98	114
1-22-73	0.44	100	101
1-23-73	0.43	100	101
1-24-73	0.43	100	98
1-26-73	0.47	99	99
1-27-73	0.48	100	100
1-28-73	0.47	98	99
1-29-73	0.45	97	96
1-30-73	0.43	99	98
1-31-73	0.45	96	101
2-1-73	0.47	99	113
2-2-73	0.48	99	111
2-3-73	0.48	99	114
2-4-73	0.46	99	114
2-5-73	0.45	99	111
2-21-73	0.46	102	116
2-22-73	0.50	102	116
2-23-73	0.50	102	120
2-24-73	0.47	102	116
2-25-73	0.44	102	118
2-28-73	0.48	102	114
3-1-73	0.52	99	113
3-3-73	0.50	102	111
3-4-73	0.52	101	111
3-5-73	0.46	101	111
3-6-73	0.45	100	110
3-9-73	0.49	102	115
3-10-73	0.50	102	116
3-11-73	0.47	102	118
3-12-73	0.48	102	118
3-13-73	0.49	101	113
3-14-73	0.48	97	105
3-15-73	0.50	98	113
3-16-73	0.48	98	113
3-17-73	0.47	98	109
3-18-73	0.46	98	109
3-19-73	0.47	99	108
3-20-73	0.50	97	108
3-21-73	0.48	98	108
3-23-73	0.50	99	108
3-24-73	0.48	98	110
3-25-73	0.46	99	111

SECTION X

QUANTITIES AND COSTS BASED ON CONDITIONS DURING THE PROJECT

During the two-year project, 172,040,000 gallons of water was processed to load 1,643,700 pounds of carbon with 407,890 pounds of COD. This resulted in an average carbon loading of 0.25 pounds of COD per pound of carbon. The carbon was used as the rate of 9.5 pounds per 1000 gallons of water treated. The average feed COD was 249 ppm and the average effluent was 50 ppm. Averaged data for each of the three periods of operation is given in Table 9.

The data in Table 9 shows that the second rains single stage operation had a slightly higher loading than the first rains single stage operation, and a lower effluent COD.

The overall average cost to operate the plant was 49C per 1000 gallons of water treated, or 24¢ per pound of COD removed from the water. The cost summaries are given for both years' operation in Table 10.

As can be seen in Figure 10, the cost was greatly reduced the second year of operation due to improvements in the system. The operating labor and carbon costs remained close to the same while the repair labor and utilities costs accounted for the major decrease.

With the improved operation of the second year, the plant demonstrated the ability to operate at only 40¢ per 1000 gallons of water treated, or 18¢ per pound of COD removed.

Table 9. ADSORPTION DATA

	FEED COD, ppm		EFFLUENT COD, ppm		CARBON LOADING lb. COD/lb. carbon	
	AVERAGE	HIGH	AVERAGE	HIGH	AVERAGE	HIGH
FIRST RAINS - SINGLE STAGE	377	490*	67	158	0.23	0.30
TWO STAGE TEST RUN	235	395	47	105	0.22	0.39
SECOND RAINS - SINGLE STAGE	233	345	48	95	0.26	0.39
TOTAL	249	490*	50	158	0.25	0.39

*The high value of 490 ppm COD is based on the assumption that the peak of 900 ppm COD during run 5 of the first rains is invalid.

TABLE 10

COST DATA

COST AREAS	First Year $	First Year Cents Per Thousand Gallons Of Water Treated	First Year Cents Per Lb. of COD Removed	Second Year $	Second Year Cents Per Thousand Gallons Of Water Treated	Second Year Cents Per Lb. of COD Removed	Total $	Total Cents Per Thousand Gallons Of Water Treated	Total Cents Per Lb. of COD Removed
UTILITIES	12209	17	9	8859	9	4	21067	11	5
REPAIR LABOR	7553	11	6	2698	3	1	10251	5	3
OPERATING LABOR	8470	12	7	14973	15	7	23443	13	7
CARBON	10247	15	8	11532	11	5	21779	13	6
MISCELLANEOUS*	5113	7	4	2136	2	1	7249	4	2
TOTAL	43592	62	34	40197	40	18	83789	46	23

*MISCELLANEOUS INCLUDES:

1. Maintenance overhead
2. Transportation overhead
3. Maintenance costs other than labor

SECTION XI

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APPENDIX A

TEST METHODS USED FOR ANALYSIS OF WATER

HIGH LEVEL COD

The method given below is a brief summary of EPA STORET No. 00340 taken from Methods for Chemical Analysis of Water and Wastes 1971, Environmental Protection Agency Water Quality Office, Analytical Quality Control Laboratory, Cincinnati, Ohio. p.17.

HIGH LEVEL WET COD
(50 mg/l & higher)

APPARATUS

500 ml flat bottom boiling flasks 24/40

Condensers - 300 mm Liebig or equivalent

Hot plates - 9 watts/in^2

REAGENTS

0.25 N $K_2Cr_2C_7$ (Containing 120 mg Sulfamic acid/liter to eliminate nitrite N interference up to 6 mg/l N in a 20 ml sample)

Conc. H_2SO_4 + 22 mg $AgSO_4$/9# bottle

0.10 N $Fe(NH_4)_2(SO_4)_2.6H_2O$ (40 gm FAS + 20 ml conc H_2SO_4 diluted to 1 liter)

Ferroin Indicator

$HgSO_4$

PROCEDURE

1. Place approximately 0.4 gm $HgSO_4$ and a few glass

beads in a 500 ml boiling flask.

2. Add 20 ml of sample of aliquot + H_2O.

3. Pipette 10 ml 0.25 N $K_2Cr_2O_7$ into the boiling flask and connect it to the water cooled condenser.

4. Slowly pour 30 mls H_2SO_4 + AG_2SO4 down the top of the condenser while swirling the boiling flask. (CAUTION wear safety glasses and rubber gloves) Reflux for 2 hours (or less if sufficient).

5. Cool and wash condenser down with distilled water (90 mls).

6. Remove flask from condenser and cool to ambient temperature. Add 2-3 drops Ferroin indicator.

7. Titrate to Organge-Brown color with 0.10 N FAS which has been recently standardized.

8. Run blank with 20 mls distilled water and all reagents.

$$\text{COD mg/l} = \frac{(A-B)C \times 8000}{\text{mls sample}}$$

Where A = mls 0.10 N FAS for blank
B = mls 0.10 N FAS for sample
C = Normality of FAS

STANDARDIZATION OF FAS

1. Pipette 10 mls K_2Cr_2O7 into a 500 ml boiling flask and dilute to 100 mls.

2. Add 30 mls conc. H_2SO4 without Ag_2SO4. Cool and titrate with FAS.

$$\text{Normality FAS} = \frac{2.5}{\text{mls FAS}}$$

LOW LEVEL COD

The method given below is a brief summary of EPA STORET No. 00335, taken from Methods for Chemical Analysis of Water and Wastes 1971 Environmental Protection Agency Water Quality Office, Analytical Quality Control Laboratory, Cincinnati, Ohio, p. 19.

LOW LEVEL WET COD
(5 mg/l to 50 mg/l)

APPARATUS

500 ml flat bottom boiling flasks 24/40

Condensers - 300 mm Liebig or equivalent

Hot plates - 9 watts/in^2

REAGENTS

0.025 N $K_2Cr_2O_7$

Conc. H_2SO_4 + 23.5 gm $AgSO_4$/9# bottle

H_gSO_4

Ferroin Indicator

PROCEDURE

1. Place 1 gm H_gSO_4 + 5.0 ml conc. H_2SO_4 and a few glass beads in a 500 ml boiling flask.

2. Place in ice bath and add 25 ml of 0.025 N $K_2Cr_2O_7$ and 70 ml Conc. H_2SO_4 (with A_gSO_4).

3. Add 50 ml of sample or aliquot + H_2O.

4. Apply heat to flask and reflux for two hours.

5. Cool and wash condenser down with distilled water (25 ml).

6. Remove flask from condenser and cool to ambient temperature. Add 8 to 10 drops of Ferroin indicator.

7. Titrate to reddish hue with 0.025 $Fe(NH_4)_2(SO_4)_2$ $6H_2O$

8. Run blank with 50 ml of distilled water and all reagents.

$$\text{COD mg/l} = \frac{(A-B)\ C \times 8000}{S}$$

Where A = mls 0.025 N $Fe(NH_4)_2(SO_4)_2$ for blank
B = mls 0.025 N $Fe(NH_4)_2(SO_4)_2$ for sample
C = Normality of $Fe(NH_4)_2(SO_4)_2$
S = mls of sample

AQUARATOR COD

The theory of the AquaRator is given below. The operation of the instrument is not given in this report, but is given in "LIRA INFRARED Analyser Model 300, Theory - Operation and Service Manual" Mine Safety Appliances Company, 201 North Braddock Avenue, Pittsburg, Pennsylvania.

Theory of Operation

Quoted from "Lira Infrared Analyser Model 300, Theory - Operation and Service Manual" Mine Safety Appliance Company, 201 North Braddock Avenue, Pittsburg, Pennsylvania, pp. 10, 11.

The LIRA is based on the principle of infrared absorption. It is a common physical fact that all molecules, with the exception of elemental gases, exhibit characteristic absorption spectra that is related to the number

configuration, and type of atmos in this molecule. The more simple the molecular structure, the simpler the absorption spectrum and conversely, heavy complicated molecules exhibit quite complex spectra

By examination of the infrared spectra of the components in a process stream, it is normally possible to locate an infrared absorption band unique to the "component of interest." The LIRA detector gas, filter gas, interrupter and window materials are selected so that the optics are sensitized ("tuned") only to this unique absorption band of the "component of interest." The cell length is determined by the intensity of the absorption band and the calibration range of the instrument. LIRA optics and sensitizations are in good agreement with the "Lambert-Beer" law of light absorption.

In general, the LIRA sources direct two identical infrared beams through two parallel, gold plated, polished stainless steel gas cells housed in a solid aluminum block. One cell contains a known comparison gas, the other the sample (unknown) gas. After the radiation beams pass through the gas cells they are directed into a single detector unit that contains a sealed-in gas. As the gas in the detector absorbs infrared radiation, there is a temperature and resulting pressure increase of the detector gas. The increased pressure moves a sensitive membrane in the detector unit. The movement results in a capacitance change in the detector and this capacitance change is converted to an output signal by the electronic amplifier.

Between the infrared sources and the gas cells, a half-circle interrupter element or beam-chopper rotates at two cycles per second. As it rotates, it alternately blocks the infrared radiation beam from each source, permitting only one beam at a time to pass through the gas cells and enter the detector unit. The detector thus alternately responds to the infrared adsorption of the gases in each cell. As long as the energy at the detector is equal in both beams, a properly aligned instrument will read zero.

When the gas to be analyzed (the "component of interest") is introduced into the sample cell, it absorbs some of the detectable infrared energy and thus reduced the beam radiation that reaches the detector unit from the sample cell. As a result, the two beams become unequal and the radiation entering the detector flickers as the beams are alternated. (The brighter comparison gas beam, then the dimmer sample gas beam, etc.)

The detector gas expands and contracts with this flicker and directly indicates the energy difference between the two beams. This variation generates an electrical signal which is proportional to the infrared energy difference between the two beams.

The electronic circuit is tuned so that only variations between the intensity of the beams entering the detector unit produce an output signal. When the beams are unequal the instrument produces an output signal that can be measured. The output signal is quickly read (90% of final reading within 5 seconds) on the meter or transcribed on an auxiliary recorder.

Selectivity to the "component of interest" is obtained by (a) the detector gas, (b) window and interrupter materials, and (c) filter gases. These sensitizing components and sample cell lengths vary with the application. Most LIRA Model 300 Analyzers will operate on gains 2, 3, or 4, but some special high sensitivity applications will perform adequately on gain position 5.

SUSPENDED SOLIDS AND VOLATILE SOLIDS

The method given below is a brief summary of the Suspended Solids and Volatile Solids test given in Standard Methods for the Examination of Water and Wastewater, 13th Edition, P 538, Method 224D (1971). The equipment and furnace temperature are altered slightly from the cited method.

Equipment: Milipore Filter Apparatus

Crucibles

Glass Fiber Filters - Reeve Angel 4.25 cm Grade 934 AH

Procedure:

1. Dry crucible and glass filter in 103°C oven and place in dessicator to cool. Obtain tare weight (A).
2. Place glass filter on Millipore filter apparatus and vacuum 20-50 mls of sample through filter.
3. Rinse any adhering material from sides of Millipore filter apparatus with distilled water.
4. Dry glass filter in a 103°C oven for 2 hours.
5. Cool in a dessicator and weigh (B).

$$\text{SUSPENDED SOLIDS ppm} = \frac{(B-A) \times 10^6}{\text{mls sample}}$$

6. Place crucible and filter in 600°C (1112°F) Furnace for 10 minutes.

7. Cool in a dessicator and reweigh (C).

$$\text{VOLATILE SUSPENDED SOLIDS} = \frac{(B\text{-}C \times 10^6)}{\text{mls sample}}$$

TOTAL OIL

The total oil was determined by APRA Standards, Part 137: Petroleum Ether Extraction, 13th Ed., pp 254-257.

TURBIDITY

The turbidity was determined using a Hach Turbidimeter using Jackson turbidity units.

COLOR

The color was measured by ASTM D-1209 using cobalt-platinum color standard.

ODOR

The odor was measured by APHA, Part 136: Odor.

MISCELLANEOUS TEST RESULTS

The total oil and Suspended Solids test were run on a regular basis along with the pH. The laboratory data from January 1973 is given in Table 1. This data is typical of that obtained throughout the project.

APPENDIX A

Table 1. LAB DATA FOR ADSORPTION PLANT DURING SECOND RAINS

DATE	STREAM	PH	COD	TOTAL OIL	SUSPENDED OIL
1-18-73	FEED	7.2	320		29
	EFFLUENT	6.9	95		12
1-19-73	FEED	7.2	245	34	16
	EFFLUENT	7.1	25	1	10
1-20-73	FEED	7.0	265	27	24
	EFFLUENT	6.8	25	9	12
1-21-73	FEED	7.0	335	29	35
	EFFLUENT	7.2	20	13	17
1-22-73	FEED	7.1	335	18	17
	EFFLUENT	7.1	20	11	14
1-23-73	FEED	6.9	345	23	27
	EFFLUENT	6.6	50	6	17
1-24-73	FEED	6.8	295	20	14
	EFFLUENT	6.7	40	17	9
1-25-73	FEED	7.4	270	26	16
	EFFLUENT	7.3	50	6	8
1-26-73	FEED	6.8	260	29	16
	EFFLUENT	6.8	45	7	11
1-27-73	FEED	7.1	250	32	51
	EFFLUENT	6.9	70	16	15
1-28-73	FEED	6.8	240	22	15
	EFFLUENT	6.8	55	8	2
1-29-73	FEED	6.8	220	19	14
	EFFLUENT	6.8	55	7	3

Table 1 (cont'd). LAB DATA FOR ADSORPTION PLANT DURING SECOND RAINS

DATE	STREAM	PH	COD	TOTAL OIL	SUSPENDED OIL
1-30-73	FEED	7.1	205	32	20
	EFFLUENT	7.1	50	16	6
1-31-73	FEED	7.0	175	53	23
	EFFLUENT	7.1	40	41	4

APPENDIX B

TEST METHOD USED FOR ANALYSIS OF CARBON

RELATIVE EFFICIENCY

The method given below is the relative efficiency test developed by Atlantic Richfield Company.

RELATIVE EFFICIENCY TEST FOR ACTIVATED CARBON

1. About five grams of each carbon sample to be analyzed is oven-dried for three hours at 110°C.

2. Upon cooling to room temperature, each sample is individually ground to yield a few grams of +325 mesh powder.

3. One gram (± 0.01 gm) portions of each sample is mixed with a 50 ml aliquot of standard solution (COD concentration = A ppm) in 125 ml Erlenmeyer flasks. The flasks are well stoppered and shaken for one hour on a laboratory shaker.

4. After shaking, the COD of the aqueous phase is measured (B ppm).

5. The 100% efficiency reference is provided by treating a virgin sample of activated carbon according to steps 1 through 4.

6. The relative efficiency is calculated as

$$\text{Relative Efficiency, \%} = \frac{\frac{(A-B)}{A}}{\frac{(A-B)}{A}} \begin{matrix} \text{Sample} \\ \text{Reference} \end{matrix}$$

APPARENT BULK DENSITY

The method given below is the Apparent Bulk Density test used during the project.

APPARENT DENSITY TEST

EQUIPMENT REQUIRED

1. Vibrator Feeder - See Figures 1 through 3.
2. Cylinder, graduated, capacity 100 ml.
3. Balance having a sensitivity of 0.1 g.

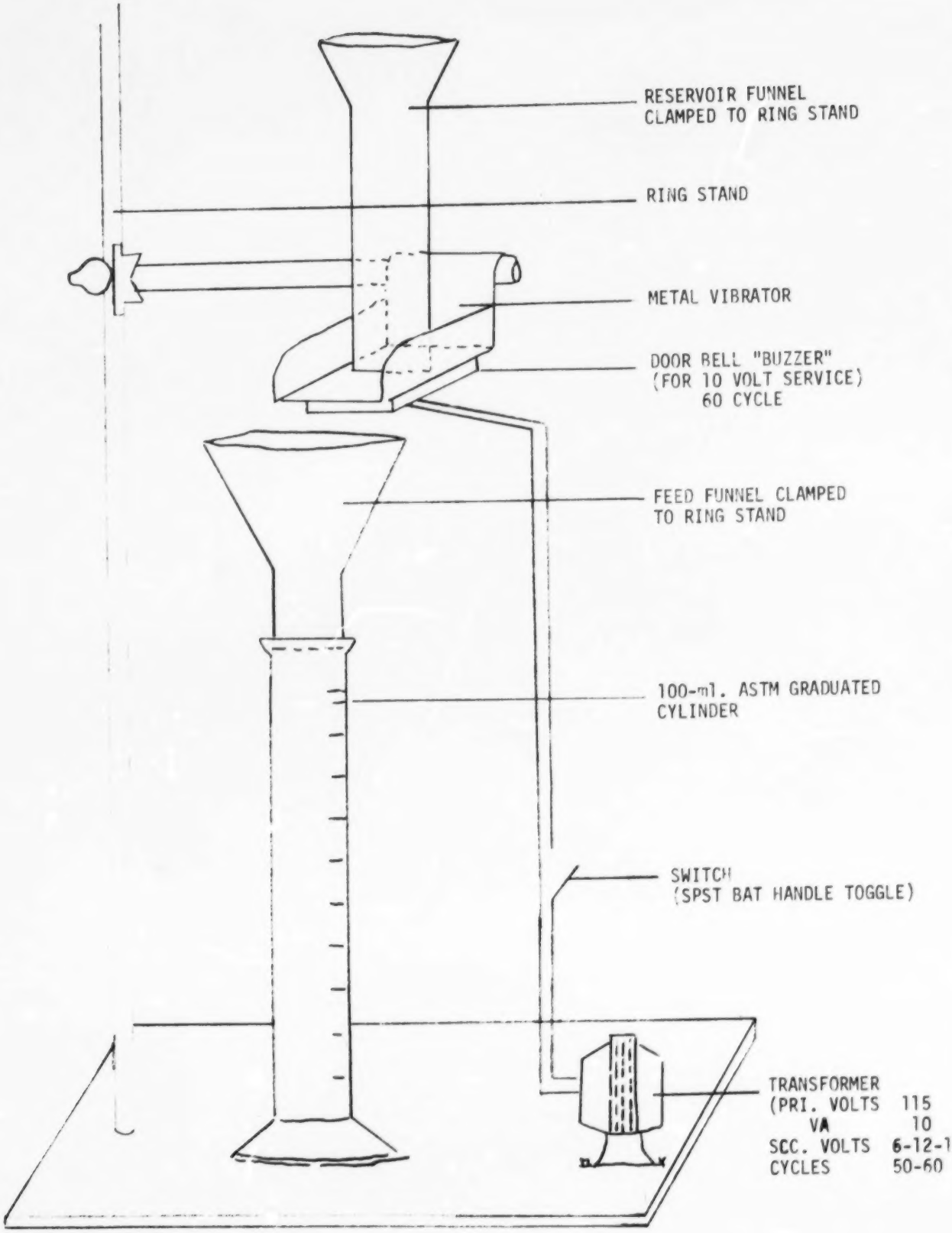
PROCEDURE

1. 100 ml. of the carbon is dried to constant weight at 150 ± 5°C or taken dry from furnace discharge chute.
2. Sample is placed into the reservoir funnel so that the material does not prematurely flow into the graduated cylinder.
3. The sample is added to the cylinder from the vibrator feeder through the feed funnel.
4. Fill the cylinder at a uniform rate of 0.75 to 1.0 ml. per second, up to the 100 ml mark. The rate can be adjusted by changing the slope of the metal vibrator and/or by raising or lowering the reservoir funnel.
5. Transfer the contents from the cylinder to a balance pan and weigh to the nearest tenth of a gram (0.1g).

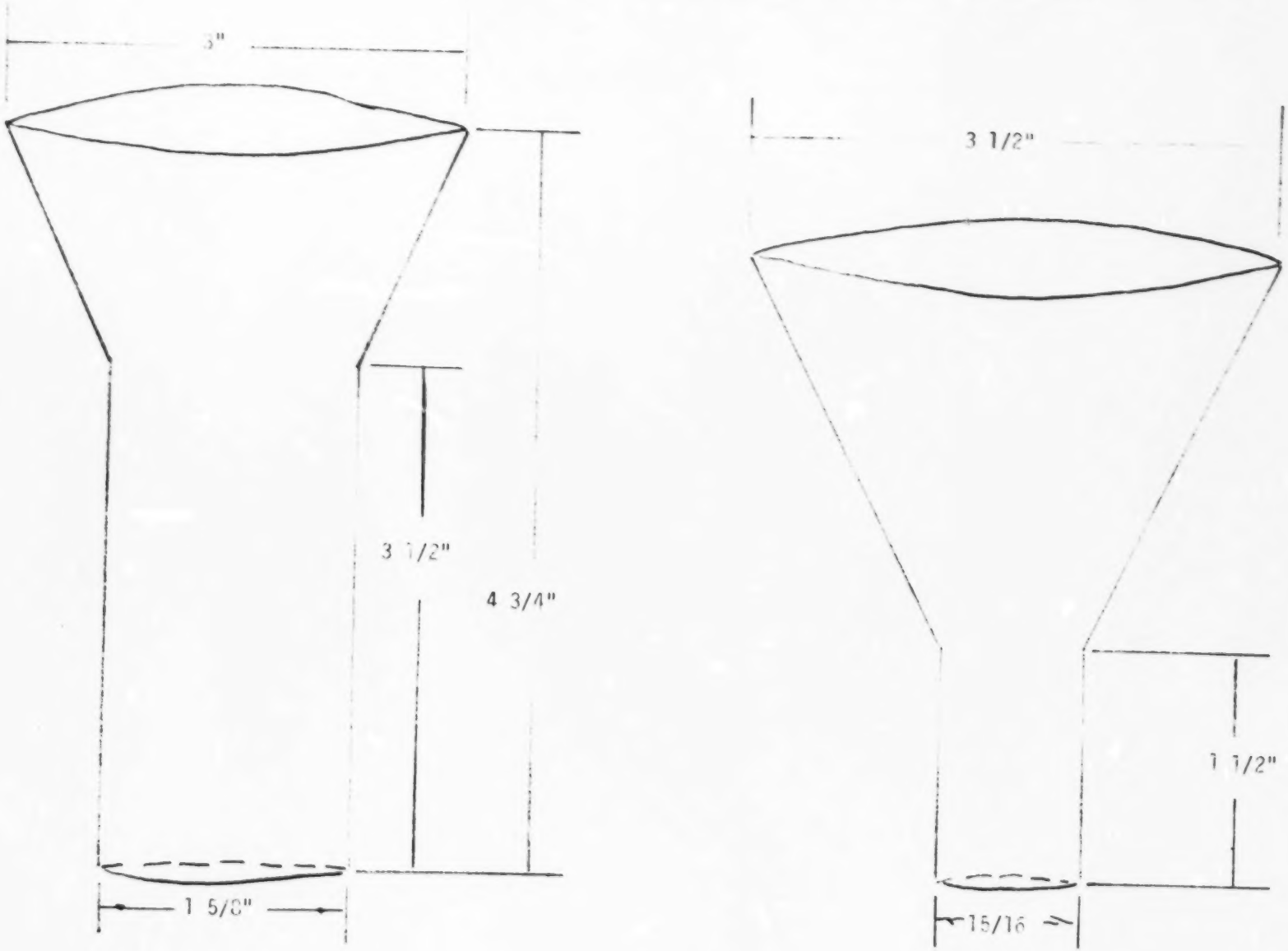
CALCULATIONS

Calculate the apparent density as follows:

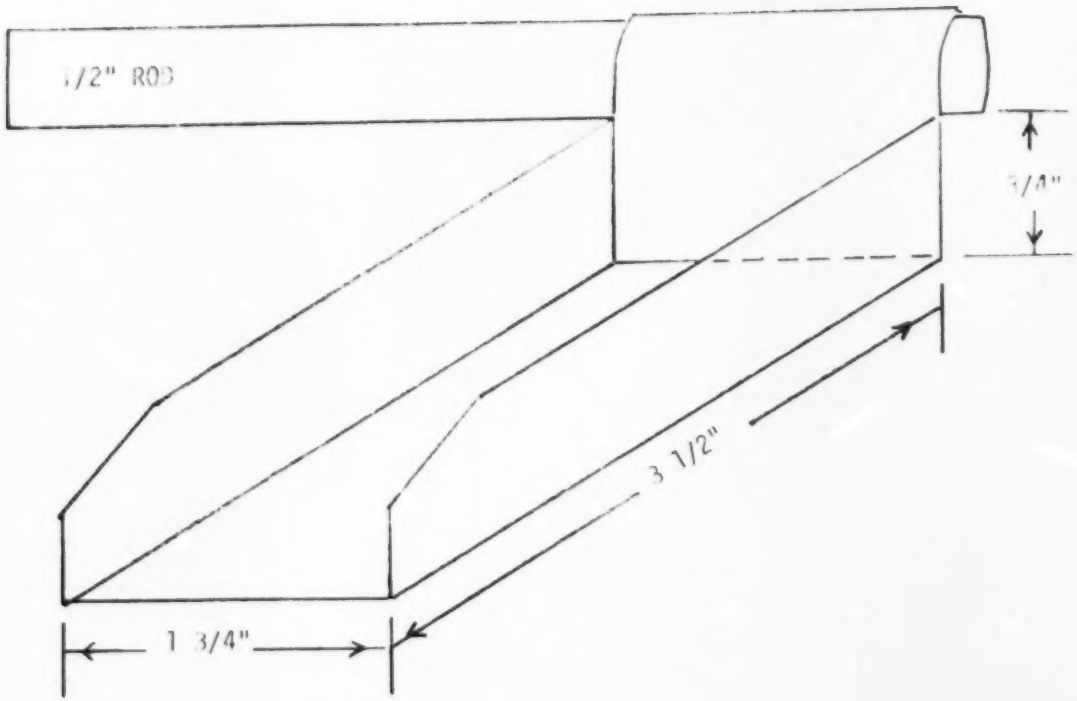
$$\text{Apparent Density, g/ml} = \frac{\text{weight of activated carbon-gm}}{100}$$



Appendix B, Figure 1. Apparent Density Vibrator Feeder



Appendix B, Figure 2. Conditions: - Glass or Metal



Appendix B, Figure 3. Metal Vibrator - 26 Gauge Galvanized Sheet Metal

APPENDIX C

DETERMINATION OF COD MATERIALS

On April 17, 1973, the United States Environmental Protection Agency in a report to Mr. Leon H. Myers, Chief, Petroleum-Organic Chemicals Wastes Section, Treatment and Control Technology Branch; from Mr. Billy L. DePrater, Supervisory Research Chemist, Petroleum-Organic Chemicals Wastes Section, Treatment and Control Technology Branch, gave the results of numerous tests on various Watson Carbon Plant streams. These tests included an attempt at a determination of the types of COD involved in the feed and effluent. The report is given below.

The numerous gas chromatographs referred to are not given in this report, and interested readers are referred to the original report.

EPA INTERNAL REPORT
ORGANICS IN ARCO SAMPLES

The organics were extracted from the Arco samples for analyses by gas chromatography to obtain a "finger-print" of the organics present and also to measure the amount of organics as determined by the area under the chromatograms.

The procedure for extraction of the water samples was to measure 500 ml of sample (750 ml in the case of "Eff New Cell") into a two liter separatory funnel and add 20 ml of redistilled chloroform. After shaking about two minutes the phases were allowed to separate, and the chloroform phase was drained into a small column of sodium sulfate which had been washed with

chloroform. The sodium sulfate column removed water and broke any emulsion that was present. Two more extractions were made on the sample using 15 ml of chloroform each time, so that the total volume of chloroform used was 50 ml.

After extracting the water samples, the extracts were concentrated by evaporating the chloroform with a gentle stream of air until the solutions were concentrated enough to run gas chromatographic analyses. The two effluent extracts contained a very small amount of organics, so the chloroform was evaporated until the volume of each was 0.1 ml. The other extracts were sufficiently concentrated after evaporation of the chloroform to a remaining volume of 1 ml.

Samples of spent carbon and regenerated carbon were extracted in a Soxhlet extraction apparatus. The spent carbon first was placed in a shallow pan on a steam bath to evaporate the water. After two hours the spent carbon appeared to be dry so samples of about 100 ml of each carbon was weighed and put into the extractors with glass wool at the bottom to prevent carbon particles from getting into the siphon tubes. Each flask contained 300 ml of chloroform and steam was used to heat the flasks and maintain a cycling rate of four times per hour for 24 hours. The extracts were then distilled to reduce the volume from 300 down to 50 ml before analysis by gas chromatography.

Gas chromatographic analyses were run with a 6' x 1/8" stainless steel, Dexsil 300 column. The temperature was programmed from 50 to 350°C at eight degrees per minute, and an electronic integrator was used to

measure the total area under the chromatogram for quantitation of the sample. Solvent oil mixtures were used for calibration by running mixtures containing 0.06, 0.12, and 0.24 mg of oil. The area measurements obtained were plotted versus the milligrams of sample. A mixture of n-paraffins was run under identical conditions to indicate the boiling range of the samples by the chromatograms. Data from the area of the chromatogram, volume of water extracted (or grams of carbon extracted), volume of concentrated extract, and volume charged to the gas chromatograph gave the following information:

Eff. New Cell	0.63	mg oil/liter
Carbon Plant Total Eff.	1.73	" " "
Carbon Plant Total Feed	34.8	" " "
Carbon Plant Total Feed	34.3	" " "
Res 505	111	" " "
Feed to Res 505	68.8	" " "
Spent Carbon	19	mg oil/gm.
Regenerated Carbon	0	" " "

Copies of the chromatograms are attached. The total area between four minutes and 42 minutes was measured using the baseline set at the beginning of the run. Corrections were made for area due to the solvent tail and drift due to stationary phase bleed that occurs toward the end of the run.

The following observations are made by comparison of Eff. New Cell and Carbon Plant Total Eff. chromatograms.

It is obvious that the carbon plant total effluent contains a greater amount of organics since the chromatograph is higher above the baseline throughout most of the run. The prominent peak at 28 minutes retention time is very likely a phthalate compound used as a plasticizer in the liner of the screw cap on the container.

The caps were supposed to have Teflon liners, but appeared to be only a Teflon coating which apparently was not impervious to the chloroform solvent. The carbon was less efficient for removing the organic compounds represented by peaks at 12 and 12.4 minutes retention time.

The composition of the organics remaining after carbon treatment consists of a higher percentage of high boiling compounds when compared to the organics in the feed. This is illustrated by plotting corrected area percentages of the total area between four and 42 minutes retention time on the chromatograms for carbon plant total effluent and carbon plant total feed. The plots show that 70 percent of the organics in the feed have a retention time of less than 22 minutes or boil below 657°F. The 70 percent point of the effluent is at about 28.8 minutes retention time or about 789°F.

If a visual comparison of peaks and areas is made, it must be remembered that the effluent sample-solvent volume was 0.1 ml while the feed sample-solvent volume was 1 ml. There is a factor of two difference in attenuation on the feed and effluent chromatograms or a total magnification of 20 on the effluent chromatogram. Several normal paraffin retention times obtained from the temperature calibration runs are shown on the feed and effluent chromatograms, and it is noted that they correspond closely to some of the sample peaks.

All of the chromatograms may be compared on the basis of peak retention times and approximate boiling points and boiling ranges; but as noted before, visual area comparisons and peak height comparisons must take into consideration the attenuation and concentration of the sample.